### Terra Rarae 2009

**An Open Access Journal**

<table>
<thead>
<tr>
<th>Sc</th>
<th>Y</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>Tb</td>
<td>Dy</td>
<td>Ho</td>
<td>Er</td>
<td>Tm</td>
<td>Yb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lu</td>
<td>Ac</td>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
<td></td>
</tr>
<tr>
<td>Cm</td>
<td>Bk</td>
<td>Cf</td>
<td>Es</td>
<td>Fm</td>
<td>Md</td>
<td>No</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Proceedings of ICfE-7**

7th International Conference on f Elements

Cologne, Germany

23-27 August 2009

Gerd Meyer, editor

NWT-Verlag
Terrae Rarae 2009  An open access journal

Gerd Meyer (Editor)

Proceedings of the 7th International Conference on f Elements (7 ICfE), incorporating XXII. Tage der Seltenen Erden, Cologne, Germany, August 23-27, 2009

1st edition 2010
ISSN

NWT-Verlag, 53332 Bornheim
www.nwt-verlag.de

Printed in Germany
## Contents

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>L. R. Morss</td>
<td>Synthetic Milestones in f Element Inorganic Chemistry</td>
<td>01, 1-6</td>
</tr>
<tr>
<td>V. Kiisk, T. Kangur, T. Tätte, I. Sildos</td>
<td>Spectroscopic properties of europium-doped TixSn1-xO2</td>
<td>02, 1-5</td>
</tr>
<tr>
<td>A. Kedziorski, L. Smentek</td>
<td>Theoretical Description of the Energy Transfer in Lanthanide Materials</td>
<td>05, 1-10</td>
</tr>
<tr>
<td>P. Pal, H. Hagemann</td>
<td>Luminescence of Sm²⁺ Doped in BaFBr</td>
<td>06, 1-2</td>
</tr>
<tr>
<td>G. Oczko</td>
<td>Investigation of Lanthanide(III) Coordination Compounds with 4-Pentenoic and 3-Butenoic Acids</td>
<td>08, 1-11</td>
</tr>
<tr>
<td>E. Hemmer, T. Yamano, H. Kishimoto, K. Soga</td>
<td>Cytotoxicity of Gd₂O₃:Ln³⁺ Nanostructures and their Potential as Biomarkers</td>
<td>09, 1-10</td>
</tr>
<tr>
<td>I. Hartenbach</td>
<td>Rare-Earth Metal(III) Chloride ortho-Oxomolybdates(VI): One Formula REC[MoO₄] (RE = Y, La – Nd, Sm – Lu) but Four Structure Types</td>
<td>12, 1-7</td>
</tr>
<tr>
<td>J. Hölsä, T. Laamanen, M. Lastusaari, P. Novák</td>
<td>Structure Optimization and Electronic Structure of the SrAl₂O₄:Eu⁺⁺ Persistent Luminescence Material by DFT Calculations</td>
<td>13, 1-6</td>
</tr>
<tr>
<td>J. Hölsä, A. Kotlov, T. Laamanen, M. Lastusaari, M. Malkamäki, P. Novák</td>
<td>Synchrotron Radiation Studies of Rare Earth Persistent Luminescence Materials</td>
<td>14, 1-8</td>
</tr>
<tr>
<td>Author(s)</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>-----------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>J. Hölsä, H. Jungner, M. Lastusaari, M. Malkamäki, J. Niittykoski</td>
<td>Effect of Grinding on the UV Excited and Persistent Luminescence of SrAl$_2$O$_4$:Eu$^{3+}$,Dy$^{3+}$</td>
<td>15</td>
</tr>
<tr>
<td>I. Hyppänen, J. Hölsä, J. Kankare, M. Lastusaari, L. Pihlgren, T. Soukka</td>
<td>Preparation and Up-Conversion Luminescence Properties of NaYF$_4$:Yb$^{3+}$,Er$^{3+}$ Nanomaterials</td>
<td>16</td>
</tr>
<tr>
<td>N. S. Hillesheim, J. Sundermeyer</td>
<td>Unexpected sp$^3$ C-H Activation Upon Metallation of a New Cyclopentadienyl-N-silylphosphazene Ligand by the Yttrium Triaryl [Y(dmba)$_3$]</td>
<td>17</td>
</tr>
<tr>
<td>T. Grzyb, M. Weclawiak, S. Lis</td>
<td>Synthesis and Photophysical Properties of LaOF:Eu$^{3+}$ Nanocrystals</td>
<td>19</td>
</tr>
<tr>
<td>S. Lis, M. Kaczmarek, K. Staninski, D. Komar, M. Buczkowska</td>
<td>Chemiluminescence and Electrochemiluminescence of Lanthanide(III)/fluoroquinolone Systems</td>
<td>20</td>
</tr>
<tr>
<td>J. Hamacek</td>
<td>Self-Assembly of Polynuclear Arrays for Sensing Purposes</td>
<td>21</td>
</tr>
</tbody>
</table>
Synthetic Milestones in f Element Inorganic Chemistry

Lester R. Morss*

1000 Independence Avenue, SW, Washington, D.C. 20585-1290 / USA
E-mail: Lester.Morss@science.doe.gov

Abstract. This paper highlights the chemical ingenuity and craftsmanship of Professor Gerd Meyer and his inorganic chemistry colleagues who have extended the tradition of synthesis of pure rare earth and actinide compounds. Inorganic synthesis is an intellectual discipline that is essential to most chemical, materials science, and solid state physics research. It requires broad understanding of principles of chemical thermodynamics, kinetics, acid-base chemistry, and chemical bonding relationships, as well as specialized skills and intuition that few scientists have mastered.

Keywords: f Elements; Solid State Chemistry; Coordination Chemistry

1 Introduction

Discovery is at the heart of many scientific disciplines. The preparation of novel chemical compounds of high purity is at the heart of chemistry. Many chemists recall their proudest and most inspiring moments when they viewed beautiful crystals of a new or purified substance before their eyes. John Corbett captured the essence of synthetic inorganic chemistry in many of his papers with his phrase “First comes the synthesis.”

Chemical synthesis is both an artistic and a scientific endeavor. Rather than attempting to be comprehensive, this paper highlights the combination of artistic talent and scientific scholarship that has distinguished the essence of inorganic f-element compound synthesis as well as the careers of Gerd Meyer, his mentors, and his colleagues.

In this paper the term “lanthanides” includes all elements lanthanum through lutetium, abbreviated Ln. “Rare earths” includes Sc and Y. “Actinides” includes all elements actinium through lawrencium, abbreviated An.

2 Metals, Intermetallics, and Other Metal-Bonded Systems

The preparation of a pure chemical element in its elemental form has always been a goal of chemists and materials scientists. To reduce oxides or halides to metals, the synthetic inorganic chemist needs to select and design refractory containers and must be skillful to degas them to reduce compounds of the electropositive f elements to the pure metals. Of historical interest during the Manhattan Project, Leo Brewer’s insights led to the use of cerium sulfide to manufacture refractory containers for reduction of plutonium [1, 2]. The use of degassed tantalum crucibles for synthesis of rare earth metals was pioneered by Spedding and Daane [3]. Corbett [4], Meyer, and others extended the use of tantalum crucibles in many studies of reduced metal halides.

Synthesis of pure actinide metals requires adroitness with materials in solid, liquid, and gas phases. Neptunium metal has recently been made by reduction via electrodeposition from solution, amalgamation at a mercury cathode, and purification by distillation [5].

3 Binary compounds

Lanthanide and actinide oxides

Most chemists consider that oxides are easy compounds to synthesize, because most metallic elements form oxides in air. The term “rare earths” refers to oxodic minerals in which many of the 4f elements are found in nature. Oxides of f elements are sufficiently basic that they must be purified from carbonate from atmospheric...
CO2. The stoichiometry of many oxides, for example those of Pr, Tb, U, Cm, and Cf, varies with preparative conditions, in particular with temperature and quenching conditions.

Oxides of unusually low and high oxidation state are special synthetic challenges. Among the binary f-element oxides in the latter category, four syntheses stand out:

Sesquioxides of the lanthanides and of most actinides are very well characterized. However there are no sesquioxides of Th, Pa, U, or Np. Even Ce2O3 and PuO2 must be reduced from dioxide via conproportionation with metal or other reductants at 1500 °C or higher. This may seem surprising because the trivalent aqueous ions Ce3+, U3+, Np3+, and Pu3+ and many trivalent compounds of these elements are well known. The reason for the synthetic obstacle is thermodynamic as well as kinetic: the fluoride-structure dioxides are both very stable (creating miscibility gaps between An and AnO2 in the Th-Np oxide phase diagrams) and very inert (requiring high temperatures to achieve solid-solid reactions). The marginally stable sesquioxides Ce2O3 and Pu2O3 (with respect to disproportionation) can only be synthesized under exotic high-temperature conditions [6-8].

Neptunium pentoxide: The stoichiometry and all other properties of the highest neptunium oxide was unknown for several decades. Neptunium pentoxide, Np2O5, was prepared by several unusual routes. Finally single crystals were synthesized recently under mild hydrothermal conditions [9], a relatively new tool in the synthetic chemist’s toolbox.

Hyperstoichiometric plutonium dioxide. PuO2+x, was probably seen by many plutonium scientists in colorful “dioxide” samples prepared by various routes [10]. Haschke et al. [11] succeeded in convincing most of the world’s actinide chemists that PuO2+x with x ≤ 0.3 really can be produced by careful reaction of PuO2 with water vapor or moist air at about 350 °C.

Monoxides. Other than EuO, Eu2O3, and possibly YbO, there are no stable solid f-element monoxides [7]. Synthesis of EuO and Eu2O3 requires reducing high-temperature conditions similar to those for Ce2O3. Metastable solid monoxides of several other lanthanides have been synthesized from a mixture of metal and sesquioxide at high pressures (15-80 kbar and 500-1200 °C). These monoxides are metallic in character, with electronic structures represented as (Ln3+)O2-(e-). Upon rapid cooling they do not disproportionate. They are metastable at room temperature but stable at high pressure because the molar volume of the solid product (Ln3+)O2-(e-) is less than that of the solid reactants (LnO1.5 + 0.5Ln), i.e. there is a negative PAV term in the free energy that makes the free energy of the conproportionation reaction favorable (negative) at high pressure.

Monoxides, dioxides, and trioxides of most lanthanide and of many actinide elements are known in the gas phase. Although there are reports of solid monoxides of some actinides (in particular UO, NpO, PuO, and AmO) the reports are usually based on X-ray powder patterns of rock salt structures that in some cases have been shown to be surface impurities such as oxynitrides. This author is unaware of attempts or successes to prepare bulk actinide monoxides either by vapor deposition or by high-pressure conproportionation. Such syntheses remain a challenge for the next generation of synthetic chemists.

Lanthanide and actinide hydrides

Hydrides of most f elements are best synthesized from the elements. Because the only method of synthesis is from the elements, the kinetics of the metal-hydrogen reaction at the solid-gas interface dominate discussions of syntheses [12]. For the lanthanides and for actinides Np-Cf the product is typically LnH2-x or AnH2-x where δ≤0.9 [13]. Some dihydrides have also been prepared. Protactinium and uranium form stoichiometric or nearly stoichiometric AnH3. Thorium is the only element for which a higher hydride (ThH1.5) is known.

Lanthanide and actinide trichlorides, tribromides, and triiodides

These and many other halides are very hygroscopic. Pure trihalides typically require specialized apparatus and great skill to prepare. As is the case with oxides, these and other halides are of fundamental and applied interest. Synthesis of anhydrous halides is also important because they are synthetic precursors for complex halides and organometallic compounds.

Synthetic procedures for lanthanide and actinide trichlorides are found in many places. The monograph by Brown [14] is comprehensive, describing syntheses known by 1968. The most comprehensive and recent synthetic procedures are those pioneered by Meyer [15].

Actinide hexafluorides and lower binary fluorides

Among the first hexafluoride synthesized were those of osmium and uranium [16], both from the elements. More elegant methods have been developed, but almost all use elemental fluorine. Perhaps the most elegant synthesis of a thermodynamically unstable compound is that of PtF6, made as an unstable byproduct of the combustion of Pt in the form of a hot wire with elemental fluorine [17].

© 2010 NWT-Verlag, Bornheim, Germany
Almost all hexafluoride syntheses require elemental fluorine, typically at temperatures where a significant fraction of $F_2$ is dissociated. $UF_6$ can be prepared without use of fluorine [18]:

$$UF_4 + O_2 \rightarrow UF_6 + UO_2F_2.$$ 

Synthetic procedures for lanthanide fluorides were reviewed by Brown in 1968 [13] and more recently by Müller [18a]. Synthetic procedures for actinide fluorides were reviewed by Freestone and Holloway [18b].

The pentafluorides are synthetic challenges because of their marginal stability, between stable tetrafluorides and volatile hexafluorides. Neptunium pentafluoride has been prepared from precursors [18c], the most recent being by reaction of NONpF$_6$ with LiF and BF$_3$ in anhydrous HF [19]. The precursor NONpF$_6$ is also an unusual Np(V) compound, synthesized [20] from FNO and NpF$_6$ under UV irradiation. Plutonium pentafluoride has thus far escaped synthesis, despite innovative attempts in the solid [21] and gas phase [22]. It is believed to be unstable with respect to disproportionation [18b]. However, NOPuF$_6$ has been synthesized [20] from FNO and PuF$_6$, without the need for UV irradiation.

**Halides with f-element oxidation state equal to or less than 2.0**

Reduced lanthanide halides (typically LnCl$_2$ but also sesquihalides such as Gd$_2$Cl$_3$ and ternary halides such as CsDyCl$_3$) require strongly reducing conditions. In general these are synthesized by metallothermic reduction: conproportionation of trihalide and metal (lanthanide metal for LnCl$_2$, Gd$_2$Cl$_3$, etc., or alkali metal for CsLnCl$_3$, etc.) in sealed fused silica or tantalum vessels [29, 29a]. Dihalides of Am, Cf, and Es have been synthesized by milder methods, such as reaction of Am metal with HgX$_2$ or even reduction of trihalide with hydrogen, because Am is the actinide analogue of Eu, in which the dipoitive ion is slightly stabilized by the $f^7$ electron configuration and because the actinides heavier than Bk show increasingly stable +2 oxidation states. In general these syntheses remain to be reproduced because of the difficulty in obtaining long-lived Am-Es isotopes, even in national laboratories, and in handling these isotopes on microgram or larger scale [29b].

Synthesis of Bk dihalides was attempted by a nuclear “hot chemistry” technique: observing the phase transformations upon allowing $\beta^-$ decay of the $^{249}$Bk in the $^{249}$Bk trihalides over a period of more than a year. It was conjectured that the electrons released in $\beta^-$ decay might reduce the Bk or its progeny Cf. This did not occur; the trihalides transformed into (Bk-Cf)X$_3$ solid solutions, ultimately into Cf trihalides [29c].

As is the case for monoxides, the author is unaware of bulk syntheses of any reduced (divalent) actinide halides, either binary or polynary, of actinides lighter than Am or of Cm. This is another challenge for future synthesis.

A summary of the production of reduced halides containing divalent rare earths has been published by Meyer [29d]. In his paper, dedicated to his “doctor father” R. Hoppe, he focused on metallothermic reduction as developed for the first production of rare earth metals by W. Klemm, his “doctor grandfather” and other pioneer synthetic chemists.

**4 Complex compounds**

**Polynary oxides and halides**

This section is restricted to those polynary compounds in which f-element ions of unique oxidation state or coordination have been created.

During the preparation of Li$_4$NpO$_5$ and other Np(VI) oxides, Keller et al. [23] found that some of these materials dissolved in alkaline solution to produce green solutions. They did not recognize that Np(VII) was produced. Finally in 1967 Krot and Gel’mann [24] announced the synthesis of Np(VII) and Pu(VII) in alkaline solution. Within a few years a large number of Np(VII) and Pu(VII) polynary oxides had been synthesized. Several more years were required to characterize these compounds structurally. One of the first to be discovered, Li$_5$NpO$_6$, was only partially characterized by X-ray powder diffraction because, like many complex oxides containing both low-Z and high-Z elements, only the actinide element has a high X-ray scattering factor. It was more recently characterized by neutron powder diffraction [25].

The $+3$ through $+6$ oxidation states of plutonium were established in USA during the Second World War [26]. During the Manhattan Project studies, electrolytic oxidation of alkaline solutions of Pu(VI) and chemical oxidation with Ag(II) in dilute HNO$_3$(aq) showed no evidence of further oxidation of Pu(VI) [27]. Several ternary Pu(VII) oxides are now known. Evidence for Pu(VIII) in a ternary oxide has recently been published.
Most of these polynary oxides display actinide oxidation states that are unknown in binary oxides: \( \text{Li}_2\text{PuO}_2 \) is a Pu(VI) oxide but anhydrous PuO\(_2\) is not known; \( \text{Li}_2\text{NpO}_3 \) is a Np(VII) oxide but anhydrous Np\(_2\O_7\) is not known. Thus the synthetic chemist can find new oxidation states in complex compounds that stabilize unusual metal oxidation states.

It should be noted that much interest in synthesis of rare earth complex oxides has been focused since the first announcement in 1987 of the many high-temperature superconducting (HTSC) oxides that contain Y\(_{3}\), La\(_{2}\), and other rare earths. This paper does not discuss the synthetic techniques used to prepare these compounds in polycrystalline form, as single crystals, as thin films, and as components of wires: sol-gel techniques, metal-organic chemical vapor deposition, “soft chemistry” (chimie douce) from coordination-complex precursors, spray pyrolysis, freeze drying, etc. It notes simply that many HTSC oxides required careful duplication or improved syntheses in other laboratories to establish their purity and their unique properties.

Complex f-element trichlorides, tribromides, and triiodides have been comprehensively studied, beginning with synthesis and following through to structural, spectroscopic, and electronic-structure characterization, by Meyer [28] and coworkers. He has mentored many colleagues and students in this area, including the author of this article. He reviewed the syntheses of these compounds, “dry” (from anhydrous binary halide precursors), “wet” (from aqueous or other solutions), ammonium-halide-complex, melts, or other routes [28].

Just as polynary oxides can be synthesized with higher f-element oxidation states than the corresponding binary oxides can be synthesized, unique oxidized polynary halides can be similarly synthesized. The simplest example is \( \text{Cs}_2\text{CeCl}_6 \), first synthesized in 1966 [30]. It is interesting to note that the corresponding complex chloride of plutonium was synthesized much earlier, and those of americium and berkelium later. The author has attempted but not succeeded to prepare the corresponding tetrachlorides CeCl\(_4\) and PuCl\(_4\) by inert matrix deposition and metathesis (unpublished studies). There is evidence for higher oxides and halides such as PuO\(_3\) and PuCl\(_3\) in the gas phase, so these also remain as challenges for future syntheses. A parallel exists for lanthanide tetrafluorides; only CeF\(_4\), PrF\(_4\), and TbF\(_4\) are known as pure solids whereas complex tetrafluorides of unstable Pr\(^{4+}\), Tb\(^{4+}\), and the very unstable Nd\(^{3+}\) and Dy\(^{4+}\), have been prepared by fluorination [18a, 28a].

### 5 Coordination compounds and organometallic compounds

Synthesis of the coordination complexes and organometallic compounds of the five elements is beyond the scope of this article. Because organometallic compounds usually require strictly anhydrous and oxygen-free conditions, polar solvents such as acetonitrile, Schlenk lines and inert-atmosphere box techniques are primary tools of organolanthanide and organoactinide chemists.

### 6 Concluding remarks

This paper describes how Professor Gerd Meyer and his contemporary synthetic inorganic chemist colleagues have built on the long tradition of inorganic synthesis in the area of f elements. The author is well aware of many other monographs and reference works that have been written for the synthetic inorganic chemist, in particular the Inorganic Syntheses series begun by Booth [30a]. The most recent volume in this series is volume 35 [31]. Encyclopedic treatises have been compiled by Brauer [32], Hagenmuller [33], Zuckerman and Hagen [34]. Monographs on techniques of inorganic synthesis include those by Jolly [35], Rao [36], and Herrmann [37]. The Gmelin Handbuch der Anorganischen Chemie, with multiple volumes on each element and its compounds, published until at least 1997 and still available in many research libraries, is authoritative and comprehensive. As in the case for many other disciplines, Gerd Meyer and his colleagues “have stood on the shoulders of giants.”

The tradition of synthetic chemistry is to prepare chemical substances as pure as the state of the synthetic chemist’s art will allow. This tradition was considered by some as an end in itself but nowadays the synthetic chemist is usually a member of a team motivated by the unique properties of specific chemical substances. Synthesis is typically followed by chemical analysis and structure determination. Determination of important physical properties (spectroscopic, magnetic, thermodynamic, etc.) requires that substances be sufficiently pure (including “minor” impurities that give rise to spurious magnetic or spectroscopic signals, as well as amorphous phases not detected by crystallography) that materials scientists, catalytic chemists, and engineers of many disciplines will be able to utilize these properties for productive applications.

Many chemists of the past centuries were sufficiently “generalists” rather than specialists so that they could be skilled in synthesis as well as in structure determination, and elucidation of physical properties. Synthetic chemists of this century typically work in teams. Their skills are essential to many other disciplines.
(physical chemistry, spectroscopy, materials science). It is essential that specialists in a wide range of scientific and engineering disciplines recognize and appreciate how important it is that, as John Corbett wrote, “First comes the synthesis.”

Acknowledgement. The preparation of this paper was supported by the Office of Basic Energy Sciences, US Department of Energy. The author thanks his colleagues whose comments made significant improvement in the manuscript.

References


© 2010 NWT-Verlag, Bornheim, Germany


Received: December 30, 2008.
Spectroscopic Properties of Europium-doped Ti$_x$Sn$_{1-x}$O$_2$

Valter Kiisk*, Triin Kangur, Tanel Tätte, and Ilmo Sildos

Institute of Physics, University of Tartu, Riia Str. 142, 51014 Tartu, Estonia
E-mail: kiisk@ut.ee

Abstract. Europium-doped Ti$_x$Sn$_{1-x}$O$_2$ powders were prepared by a sol-gel route. Subsequent heat treatment up to 800°C was applied. Steady-state and time-resolved photoluminescence characterization of the materials were performed by using various excitation sources. Photoluminescence spectra revealed several different sites for the impurity ion in the host depending on the Ti/Sn ratio and the crystalline phase (anatase vs. rutile). The direct excitation of europium prevailed in mixtures containing an essential amount of titania whereas mainly host-sensitized emission could be observed in materials with high tin content.

Keywords: Oxides; Solid solutions; Rare earth elements; Sol-gel chemistry; Sintering; Photoluminescence

Introduction

It is well known that several phosphors currently employed in modern lighting devices (e.g. phosphor-converted LEDs) have complicated preparation routes or stability issues. In addition, narrowband red emitters (based on Eu$^{3+}$, for example) are desired due to their higher lumen equivalent. Trivalent rare earths are also preferred due to their stability. Various oxides can be easily prepared and doped with rare earths by employing sol-gel techniques. Wide-gap semiconducting TiO$_2$ and SnO$_2$ are especially interesting as their mixture exhibits a miscibility gap at temperatures less than ~1000°C. Both oxides as well as their solid solutions are stable in the rutile phase although nanocrystalline TiO$_2$ is also easily stabilised in the anatase structure.

Europium-activated TiO$_2$ and SnO$_2$ have been quite thoroughly studied and characteristic emission patterns due to Eu$^{3+}$ are observed. Energy transfer from host to guest is suggested for TiO$_2$:Eu$^{3+}$ and SnO$_2$:Eu$^{3+}$. Hereby, additional experimental evaluation of the statements will be provided. We also pay attention to the solid solutions of TiO$_2$ and SnO$_2$ as a potentially tunable luminescence material (revealed in either emission or excitation properties of the activator). It is also of fundamental interest to apply Eu$^{3+}$ as a structural probe in this solid solution series.

Description of samples and experimental details

Five samples of Ti$_x$Sn$_{1-x}$O$_2$ (x = 0, 0.25, 0.5, 0.75, 1) with 1 at% nominal Eu concentration as well as undoped SnO$_2$ were prepared by using the sol-gel route based on hydrolysis and polycondensation of metal alkoxide.

precursors. First, proportional mixtures of neat Ti(OPr)$_4$ and Sn(OPr)$_4$ in propanol were prepared. To initiate hydrolysis of the alkoxides, 6.7% water solution in propanol, acidified by a drop of concentrated HCl, was added to the mixture. Water/alkoxide molar ratio was chosen as 0.2. For europium incorporation, suitable amount of EuCl$_3$•xH$_2$O was added to the water solution. Finally, the mixture was concentrated by using a Büchi rotator-evaporator. The viscous polymeric substance was left into air for final hydrolysis until the powder formed. After a couple of weeks of aging the powders were baked at 800°C for 1 h.

For excitation of luminescence a tunable OPO light source from Expla Ltd (pulse duration 3 ns, pulse energy ~20 µJ, repetition rate 20 Hz) was employed. The spectra were recorded by using a spectrograph (Andor SR-303i, spectral resolution 1 nm) equipped with an image-intensified charge coupled device (Andor DH-501). Luminescence excitation spectra were acquired by employing a 150 W Hamamatsu xenon lamp in combination with a monochromator (MDR-23, spectral width 2 nm). In the latter case, a Hamamatsu photomultiplier tube (H8259-01) operating in the photon counting mode was used for detection and the spectral width of the emission spectrograph was 20 nm.

The Raman spectra were recorded by using a Renishaw inVia micro-Raman spectrometer (spectral resolution 1.5 cm$^{-1}$). An argon laser emitting at 514 nm was used for excitation. About 10 mW of laser power was focused onto ~1 µm$^2$ area using 50x objective.

Results and discussion

For structural characterization of the samples, Raman spectra were recorded (Fig. 1). TiO$_2$:Eu appears to be purely in the anatase structure. For 25% and 50% of Sn content the vibrational pattern is similar to that of TiO$_2$ (rutile) whereas a higher Sn content leads to a fairly abrupt relaxation to the SnO$_2$-like rutile structure. In pure Ti$_x$Sn$_{1-x}$O$_2$ no such abrupt transitions are observed. In the present case it may be due to the europium dopant. In the spectra of Ti$_{0.75}$Sn$_{0.25}$O$_2$:Eu and Ti$_{0.5}$Sn$_{0.5}$O$_2$:Eu the weak features at 145, 250 and 315 cm$^{-1}$ may indicate traces of anatase and brookite.

In the Raman spectra of SnO$_2$:Eu and Ti$_{0.25}$Sn$_{0.75}$O$_2$:Eu, there are some additional, mainly broadband features which are hard to assign to any well-known tin compound. However, in ref. 10, where somewhat higher Eu concentrations were used, fairly strong lines typical for the pyrochlore Eu$_2$Sn$_2$O$_7$ structure are present in the Raman spectra (although they were mistakenly attributed to disorder effects). In addition, the presence of Eu$_2$O$_3$ may be suspected even for low Eu concentrations as detected via XRD. 10

Fig. 2 presents the luminescence spectra of the samples excited at 464 nm (corresponding to the $^7F_0 \rightarrow ^2D_2$ f-f transition of Eu$^{3+}$). We can see broad emission bands with a spectral intensity distribution characteristic for Eu$^{3+}$ in glasses. This emission is probably due to Eu ions in the amorphous phase between the nanocrystallites. The emission is strongest in TiO$_2$ and almost undetectable in SnO$_2$. It has been proposed that the solubility of Eu in SnO$_2$ is markedly less than 1 at%.

In general, the decay kinetics of Eu emission in an amorphous surrounding (Fig. 3) does not appear to be neither single-exponential, double-exponential nor Inokuti-Hirayama type (characteristic of energy transfer in ordered systems). For quantitative characterization of the decay curves simple two-parameter distributions of the decay constant were considered. The best fit was provided by gamma distribution which describes Becquerel-type decay law $I(t) = I_0/(1 + at)^p$. The fitting parameters ranged from $a = 0.37 \text{ms}^{-1}$, $p = 9.6$ (for TiO$_2$) to $a = 0.14 \text{ms}^{-1}$, $p = 8.8$ (for Ti$_{62.5}$Sn$_{37.5}$O$_2$) and the inverse of the mean decay constant varied accordingly from 280 to 830 ms. The so-called “stretched exponential” function $I(t) = I_0 \exp[-(t/\tau)^\beta]$, which is most frequently applied for describing relaxations in disordered systems, provides a somewhat less perfect fit where the parameter $\beta$ acquired a value around 0.81 for all samples.

Under excitation with UV radiation (355 or 266 nm) significant changes in the emission spectra take place (Fig. 4). We can see characteristic Eu$^{3+}$ emission bands with a well-resolved fine structure indicating that the Eu$^{3+}$ ions are in crystalline surrounding. Two Eu$^{3+}$ emission centers appear to be present corresponding to an anatase (TiO$_2$ sample) or rutile-like (all other samples) phase. In anatase, the $^5D_0 \rightarrow ^2F_2$ (electripole dipole) transition is prevailing whereas the $^5D_0 \rightarrow ^2F_1$ (magnetic dipole) transition is most pronounced in rutile. This can be explained by assuming that Eu ions replace the host metal cations in regular lattice positions with no charge compensating vacancies present within the first coordination sphere. In that case the point symmetry of the Eu center is $D_{2h}$ in anatase and $D_{2d}$ in rutile (ignoring the possible lattice distortion due to mismatch between the ionic radii of Eu and Ti/Sn). Therefore the lack of inversion symmetry is expected for the Eu center in anatase inducing the electric dipole transition $^5D_0 \rightarrow ^2F_2$.

The excitation spectra of the Eu$^{3+}$ emission in an amorphous surrounding (Fig. 5) indicate that the impurity is excited mainly by direct f-f absorption. However, the Eu center in rutile-type crystalline surrounding (detected via the $^3D_0 \rightarrow ^2F_1$ emission band) exposes an intense broad excitation band below 350 nm (Fig. 6). The onset of excitation corresponds closely to the band-gap of SnO$_2$ ($\sim$3.5 eV) and the excitation efficiency is highest in SnO$_2$. Therefore an efficient energy transfer from SnO$_2$ to Eu may be suspected. Note that the excitation

spectrum of Eu in a crystalline anatase surrounding could not be acquired due to the weakness of this emission and overlapping with Eu emission in the amorphous phase.

**Figure 4.** Eu$^{3+}$ emission spectra in Ti$_x$Sn$_{1-x}$O$_2$ under 355 and 266 nm laser excitation.

**Figure 5.** Excitation spectra of Eu$^{3+}$ in an amorphous surrounding.

**Figure 6.** Excitation spectra of Eu$^{3+}$ in a rutile-like surrounding.

For further evidence about the energy transfer we have measured the decay kinetics of the Eu$^{3+}$ emission under UV excitation and compared the results with the previously discussed decay of Eu in an amorphous surrounding (unfortunately the direct excitation of Eu centers in the crystalline sites could not be achieved in these samples). The decay of SnO$_2$:Eu (Fig. 7) under 266 nm excitation is extremely slow. Although an essential contribution to the longer decay may come from the lower emission rate of the prevailing $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition (~50 s$^{-1}$ according to ref. 19), the decay becomes still significantly slower at longer times suggesting that the process is limited by the excitation rather than the emission rate of the ions typical to the host-mediated energy transfer. In addition, no dependence of the decay profile on the excitation wavelength

could be noticed indicating that the excitation band is homogeneous and a single excitation mechanism is involved. In the case of TiO$_2$:Eu such a contrast between the decay curves could not be found although a marked tail is still clearly seen under 355 nm excitation (Fig. 8). Therefore it seems that if the energy transfer from host to guest takes place in TiO$_2$, it is much faster than in SnO$_2$ and is relatively inefficient considering the contrast between the excitation efficiency of TiO$_2$ and SnO$_2$ in the UV range. It is remarkable that the results for TiO$_2$:Eu are also markedly different from e.g. TiO$_2$:Sm which exposes strong host-sensitization revealed in both a pronounced excitation band above the TiO$_2$ band-gap$^{20,21}$ as well as in stretched decay kinetics.$^{21}$ It is worth mentioning that, different from ref. $^3$, efficient host-sensitized emission of Eu in amorphous titania could not be found in our samples. This may be attributed to a different nanocrystalline structure that does not favor this kind of energy transfer. Instead, relatively weak energy transfer to Eu ions in the crystalline phase is observed. Also, the use of powders instead of thin films (as in ref. $^3$) promotes the inherently weak f-f absorption in the present samples.

Conclusions

Based on spectroscopic investigations it is concluded that the sol-gel prepared Ti$_x$Sn$_{1-x}$O$_2$ solid-solution series contains three Eu$^{3+}$ emission centers located in amorphous (except for SnO$_2$), rutile-like (except for TiO$_2$) and anatase-like surrounding (only TiO$_2$). The presence of different Eu centers provides the possibility to tune the emission color from orange to red with a suitable choice of the Sn/Ti ratio and the excitation wavelength. The markedly different Eu$^{3+}$ emission spectra in anatase vs. rutile like crystalline phases were found to be in accordance with the expected site symmetry assuming the substitutional position with no charge compensating defects in the immediate vicinity of Eu$^{3+}$ ion. It appears that the local environment as experienced by the Eu ion in the rutile-like phase remains identical throughout the solid solution series. It is also concluded that, although only a relatively small amount of Eu ions seems to be incorporated into SnO$_2$ matrix, still an efficient energy transfer from the host to Eu ions takes place in Sn-containing materials below 350 nm excitation wavelength, and the excitation mechanism is homogeneous over the broad excitation band.

Acknowledgements

The authors are grateful to Mihker Rähn for assistance in Raman measurements. The Estonian Science Foundation is acknowledged for financial support (grants nos. 7456, JD69, 6999, 6658 and 7612).

Received: August 20, 2009.


Olga Snurnikova¹, Svetlana Kost¹, Natalya Rusakova¹, Stanislav Miroshnichenko², Olena Alyeksyeyeva¹, Vitaly Kalchenko², Yuriy Korovin¹*¹

¹Department of Chemistry of Lanthanides, A.V. Bogatsky Physico-Chemical Institute, 65080, Odessa, Ukraine
²Phosphoranes Chemistry Department, Institute of Organic Chemistry, 02660, Kyiv, Ukraine
E-mail: lanthachem@te.net.ua

Abstract. Complexes of terbium, europium, samarium, dysprosium and ytterbium with a number of functionalized calix[4]arenes have been obtained and their spectral luminescence properties have been investigated.

Keywords: Lanthanides; Chemistry; Coordination; Spectroscopy

Introduction

Calix[n]arenes have been widely investigated and are becoming increasingly important in the field of supramolecular chemistry, showing interesting properties and a wide range of metal coordination complexes both in solution and in the solid state.¹² In particular, the complexation of lanthanide ions by calix[4]arene ligands has been studied with the purpose of developing new luminescent probes.⁴⁻⁶ Therefore, the expansion of assortment of calix[4]arenes studied as ligands is actual and perspective.

In this paper the preliminary study of the spectral luminescence properties of lanthanide complexes (Ln = Sm, Eu, Tb, Dy, Yb) with some new calix[4]arenes which are modified by phosphorus (L₁⁻L₆) and carboxy (L₇⁻L₉) fragments (Fig. 1) are given.

Results and Discussion

The elemental analysis and spectroscopic data show that the ratio Ln:calix[4]arene = 1:1, except for complexes with ligands L₃ and L₅ (Ln:L₃(L₅) = 2:1), containing the coordinating active OH-groups simultaneously in "phenolic" and "phosphorus" centers.

The absorption spectra of calix[4]arenes L₁-L₆ and L₇-L₉ are characterized by wide split bands with \( \lambda_{\text{max}} = 270-290 \) nm (ε = 2.5-15.5×10⁴). The including of sulphur atoms in the lower rim of the macrocycle of L₃-L₅ results in a shift of the basic band of 20-25 nm (\( \lambda_{\text{max}} = 300-310 \) nm, ε =11.0-25.0×10³). It should be noted that weak intensive bands (\( \lambda_{\text{max}} = 260-270 \) nm, ε = 1.0-4.0×10³) in the short wave area of the spectra of ligands L₁-L₅ are analogous to the absorption bands of acyclic phenylphosphonates and phosphineoxides.⁷ Besides, calix[4]arene L₁ is characterized by the band in the area at \( \lambda = 330 \) nm (ε = 2.0×10³). Maximal energy of the latest corresponds to the most deprotonation form of ligand and disappears at complexation. Because the size of energy of band not depend from the lanthanide ion, it can be taken with intraligand bands of charge transfer.⁸ In the absorption spectra of ligands L₁ and L₅-L₆ is observed weak shoulder at \( \lambda = 310-320 \) nm which with the


© 2010 NWT-Verlag, Bornheim, Germany
increase of pH suffers changes (comply with acid dissociation of phenolic OH-groups). An analogical pattern is observed for mono- and dicarboxylic[4]arenes L_7 and L_8. At the same time for tetracarboxylic ligand L_9 there is an only one intensive band with a maximum at 278 nm.

Figure 1. Structures of ligands studied.

Formation of lanthanide complexes with L_1-L_9 causes the change of form, intensity and position of maxima in the absorption spectra. In particular, in the spectra of Ln-L_1, Ln-L_3 and Ln-L_9 the most wide band suffers a hipsochromical change (Δλ = 2-4 nm) with a small increase of intensity. On the whole the displacement of bands in the area of 310-315 nm (hipsochromic for Ln-L_3, Δλ = 3-4 nm and bathochromic for Ln-L_1,7,8) confirms participing of phenolic groups in complexation. In the complex Ln-L_2 the band of the calix[4]arene macrocycle (280 nm) does not suffer substantial changes while bands at 261 and 267 nm of phosphor-containing fragments (they participate in complexation) bathochromically shift by 2 nm and degenerate in shoulders. In respect of thiacalix[4]arenes L_3-L_5, then at formation of complexes there is a bathochromic change of the absorption band by 10-15 nm and an increase of the absorption intensity by 2-3 times.

The similarity between the absorption and excitation spectra of complexes indicates that an intramolecular ligand-to-metal energy transfer from the triplet (T) levels of ligands (situated at 21450-24500 cm\(^{-1}\)) to the emissive levels of Ln\(^{3+}\) takes place. It is important that, since the T-levels of the ligands are above the resonance levels of Tb\(^{3+}\), Eu\(^{3+}\), Sm\(^{3+}\), Dy\(^{3+}\) and Yb\(^{3+}\), the energy can be transferred from the excited ligands to all mentioned Ln\(^{3+}\). The efficiency of this process can be explained by the fact that the molecular luminescence of the free ligands (390-490 nm with maxima at 420-430 nm) is significantly (5-70%) reduced in their complexes with lanthanides.

It was established that a change of pH shows a highly sensitive influence on the 4f-luminescence of water-soluble complexes with L_1-L_6. It was seen that the luminescence reached its maximum when pH was 7.4-10.0. These results can be explained as follows: Tb\(^{3+}\) coordinates with the phenolic OH-groups or phosphor-containing centers. So, a suitable pH is very important for the deprotonation of ligands. In this connection pH of 7.4-8.0 for L_1-3 and 8.4-10.0 for L_4-6 was selected for further research. But it is necessary to mention that higher pH values (more than 10.0) could be the cause of the formation of insoluble Ln(OH)_3 or complexes of Ln(OH)_2^2+ and Ln(OH)_2^+ in the solution.

It is well known that luminescence intensities (I_lum) of lanthanide ions in complexes changes when travelling from one solvent to another. We have studied the influence of some solvents on the luminescence intensity of Ln-L_1-9 complexes and found that methanol affected the I_lum of complexes to a greater extent than the other organic solvents (by 2.6-3.2 times compared with acetone). The molecules of DMF and DMSO have an approximately equal effect practically in the case of all complexes. This is an unexpected fact (as coordinating centers of complexes are different) and requires further intense study. It is needed to take also into account that

namely for ytterbium complexes the emission intensities appear to strongly depend on the solvent, likely due to water re-absorption. At the same time for dysprosium and samarium complexes this effect shows up poorly.

Upon excitation at chromophoric benzene rings the 4f-luminescence spectra of terbium complexes exhibit the characteristically narrow band emissions for Tb$^{3+}$ and correspond to the $^5\text{D}_4 \rightarrow ^7\text{F}_j (J = 3-6)$ transitions (Fig. 2). The $^5\text{D}_4 \rightarrow ^7\text{F}_2$ green emission is the most prominent one. All the emission bands have shoulder peaks. But in the terbium complex with $L_1$ succeeded to be fixed only the most intensive band at 549 nm. Evidently, it is related to that is observed imposition of molecular luminescence band and short-wave band proper to the hypersensitive transition $^3\text{D}_4 \rightarrow ^3\text{F}_6$. For most of the terbium complexes there is a splitting of this band. It testifies to the change of the symmetry of complexes due to coordination of metal on the upper or lower rim of the macrocycle. It was established that the intensity of 4f-luminescence in the terbium complexes with thia-based ligands $L_4-L_6$ is substantially higher than in complexes with ligands $L_1-L_3$.

**Figure 2.** Emission spectra of Tb-$L_2$ (1), Tb-$L_3$ (2) ($H_2O$) and Tb-$L_4$ (3) (DMF) at 293 K. $C_{Lig} = 5\times10^{-5}$ M, $\lambda_{ex} = 290$ nm (1), $\lambda_{ex} = 320$ nm (2), $\lambda_{ex} = 334$ nm (3).

As can be seen in Fig. 3, the emission spectra of europium complexes contain narrow and well resolved bands which correspond to $^5\text{D}_0 \rightarrow ^7\text{F}_j (J = 0-4)$ transitions. The emission bands at 579, 592, 650 and 690 nm correspond to $^5\text{D}_0 \rightarrow ^7\text{F}_6$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions of the Eu$^{3+}$ ion. The most intense emission at 617 nm with a shoulder peak corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electro-dipole transition. The $I(^5\text{D}_0 \rightarrow ^7\text{F}_2)/I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ ratio was calculated to be 2.1, indicating that the site of the Eu$^{3+}$ ion was not located at an inversion center in the complexes.

**Figure 3.** Emission spectra of Eu-$L_9$ (1), Eu-$L_8$ (2) and Eu-$L_7$ (3) in DMF at 293 K. $C_{Lig} = 1\times10^{-4}$ M, $\lambda_{ex} = 394$ nm (1), $\lambda_{ex} = 355$ nm (2-3).

**Figure 4.** Emission spectra of Sm-$L_9$ (1) and Sm-$L_8$ (2) (DMF) at 293 K. $C_{Lig} = 1\times10^{-3}$ M, $\lambda_{ex} = 292$ nm.
Emission spectra of Sm and Dy complexes show that the same sensitization process as described for Tb and Eu complexes also occurs in these complexes with ligands L₁⁻L₉. The luminescence of samarium complexes is very weak compared to the emission of other lanthanide complexes. Its luminescence spectrum (Fig. 4) consists of four characteristic bands corresponding to the $^7G_{5/2} \rightarrow ^6H_J (J=5/2, 7/2, 9/2, 11/2)$ transitions of the Sm$^{3+}$ ion. The luminescence peak at 596 nm (non-hypersensitive transition $^7G_{5/2} \rightarrow ^6H_{7/2}$) is the strongest one.

The luminescence spectra of dysprosium complexes (Fig. 5) show only two emission peaks ($^7F_{9/2} \rightarrow ^6H_J, J=13/2, 15/2$). The luminescence band corresponding to the $^7F_{9/2} \rightarrow ^6H_{13/2}$ hypersensitive transition has the highest emission intensity. The obtained data for dysprosium complexes testify that the energy difference between the excited $^7F_{9/2}$-level of Dy$^{3+}$ and the T-states of ligands is more favorable for an efficient energy transfer than that in the samarium complexes.

![Figure 5](image_url)  
**Figure 5.** Emission spectra of Dy-L₅ (1), Dy-L₅ (2) (H₂O) at 293 K. $C_{Lig}= 1 \times 10^{-4} M$, $\lambda_{ex}= 290$ nm (1), $\lambda_{ex}= 324$ nm (2).

![Figure 6](image_url)  
**Figure 6.** Emission spectra of Yb-L₂ (1) Yb-L₄ (2) (H₂O) and Yb-L₈ (3) (DMF) at 293 K. $C_{Lig}= 1 \times 10^{-4} M$, $\lambda_{ex}= 320$ nm (1), $\lambda_{ex}= 272$ nm (2), $\lambda_{ex}= 305$ nm (3).

It should be noted that the intensity of the 4f-luminescence of europium and terbium complexes is almost of two orders of magnitude higher than for the samarium and dysprosium complexes.

Finally, in all of the ytterbium complexes luminescence at $\lambda_{max}= 980$ nm ($^2F_{5/2} \rightarrow ^2F_{7/2}$ transition) (Fig. 6) was registered.

Thus, based on the obtained data, it is possible to conclude that calix[4]arenes L₁⁻L₉ can be considered as suitable compounds for Ln$^{3+}$ ions to exhibit their metal-centered 4f-luminescence. This fact can be quite useful for design and synthesis of novel calixarene derivatives possessing the stronger sensitizing ability toward lanthanide ions.

**Experimental Section**

All starting reagents and solvents were obtained from commercial sources and used without additional purification. The synthesis of calix[4]arenes was described in other publications. It was established that calix[4]arenes L₁⁻L₉ have the "cone" conformation both in the solid state and in solutions. Obviously this conformation is stabilized by strong cooperative intramolecular hydrogen bonds. The lanthanide complexes were

---


prepared by a modified method. All ligands and complexes were isolated in the solid state and characterized by elemental analysis, IR, UV-vis, $^1$H and $^{31}$P NMR, FAB MS and luminescence spectra. The technique of identification was described by us before. Absorption spectra were recorded at room temperature with a Lambda 9 UV/Vis spectrophotometer. Emission and excitation spectra were taken on a Fluorolog FL 3-22 spectrofluorimeter (excitation source was a 450 W Xenon lamp) equipped with a photon counting system and attachment for phosphorescence measurements at 77 K. The lowest triplet-state energies of the ligands were determined by the shortest wavelength transition in the phosphorescence spectra. All spectra were corrected with a standard lamp.

**Acknowledgements**

This work was supported by the National Academy of Sciences of Ukraine (grant No. 7.0-2008).

Received: August 8, 2009.

---

Preparation of Cerium Nitride by Reaction of Cerium Hydride with Ammonia

H. Imamura*, N. Yamada, T. Kanekiyo, K. Ooshima and Y. Sakata

Graduate School of Science and Engineering, Yamaguchi University
2-16-1 Tokiwadai, Ube 755-8611, Japan
E-mail: hi-khm@yamaguchi-u.ac.jp

1. Introduction

There has been a growing interest in science and application of rare earth materials. We have studied catalytic properties of a variety of rare earth compounds.1-3,4 It has been recently found that rare earth nitrides show specific activity as catalysts; thus EuN and YbN are active as selective catalysts for the partial hydrogenation of benzene to cyclohexene.5 Europium amide, Eu(NH₂)₂, and the ytterbium amides Yb(NH₂)₂ and Yb(NH₂)₃ obtained by taking advantage of the solubility of europium and ytterbium metals in liquid ammonia are effective precursors for EuN and YbN, respectively; thus the thermal decomposition of these amides leads to catalytically active rare earth nitrides with high surface areas.4,6,7

Other rare earth metals than Eu and Yb exhibit poor solubility toward liquid ammonia, and hence a similar procedure for the preparation of rare earth nitrides cannot be adopted. For the preparation of cerium nitride, CeN, the direct reaction of cerium metal with ammonia at elevated temperatures has been previously studied, but it is difficult to prepare stoichiometric cerium nitride.6

In this study, the use of cerium amide as a precursor for cerium nitride is investigated to synthesize active nanocrystalline CeN. According to previous studies,8,9,10 there is much expectation of the synthesis of cerium amide in good yield by taking advantage of the reaction of cerium hydride and ammonia. Optimal conditions for the preparation of CeN using cerium amide thus obtained has been extensively studied by X-ray diffraction analysis (XRD) and temperature-programmed desorption (TPD) combined with mass spectrometer.

References:
2. Experimental

2.1 Procedures of sample preparation

Ce metal (99.9%) was purchased from the Santoku Co. and used in powder form by filing. Ammonia gas (Iwatani Ind. Ltd.) was purified through a calcium oxide column and subsequently through a sodium hydroxide column.

To prepare cerium hydride, the reaction of Ce metal with hydrogen was carried out with a glass apparatus provided with a high vacuum system (ca. 2.7 x 10^{-2} Pa). Prior to the reaction, the powdered Ce metal was subjected to an evacuation treatment at 473 K for 2 h, and the hydrogen absorption by the Ce metal was carried out at room temperature by introducing hydrogen gas of 0.066 MPa into a reactor with a fixed volume. The amount of hydrogen absorption was determined by change in pressure, and cerium hydride with a composition of CeH₂ was obtained.

The reaction of CeH₂ with ammonia was carried out using a planetary-type ball mill (P-6; Fritsch Ltd.), being capable of operating at 650 rpm. In a typical preparation of cerium amide, CeH₂ (0.25 g) was placed in a grinding bowl (made of zirconia; volume of 45 cm³), followed by introduction of 0.3 MPa ammonia. The mixtures were subjected to ball milling with zirconia balls (diameter: 3 mm, 55 g) for 0.25-20 h. To obtain CeN, the cerium amide thus prepared was thermally decomposed under evacuation at 300-1073 K.

2.2 Characterization

X-ray diffraction (XRD) analyses of the cerium samples obtained were conducted with a Rigaku X-ray diffractometer (RINT 2200) using Cu-Kα radiation. Temperature programmed desorption (TPD) measurements were made in vacuo at a heating rate of 3 Kmin⁻¹ by continuously monitoring desorbed gases via quadrupolar mass spectrometer. All procedures of the cerium samples were carried out without exposure to air.

3. Results and discussion

3.1 Preparation of cerium amide or cerium amide-like compounds by ball milling of CeH₂ and NH₃

For the preparation of cerium hydride, the direct reaction of the cerium metal with hydrogen gas was carried out with measuring the amounts of absorbed hydrogen. The cerium metal reacts normally with hydrogen to form the dihydride. Upon increasing the hydrogen pressure, the dihydride additionally absorbs hydrogen until a composition near trihydride is reached. The cerium hydride with the composition of CeH₂ was successfully prepared for use in the present study and the formation of CeH₂ was confirmed to have a cubic structure by XRD.

To carry out the reaction of cerium hydride with ammonia, CeH₂ thus prepared was first placed in a grinding bowl made of zirconia, followed by introduction of ammonia gas at a pressure of 0.3 MPa. The mixtures were subjected to high-energy ball milling for 0.25-20 h. As shown by time courses of changes in XRD (Fig. 1), the

![Figure 1](image_url). Time courses of changes in XRD with ball milling of CeH₂ and NH₃: (a) 0.25 h, (b) 1 h, (c) 3.5 h, (d) 7 h and (e) 20 h
cerium hydride immediately reacted with ammonia upon ball milling, simultaneously changing from dark gray to brown. The diffraction peaks corresponding to cerium hydride were considerably broadened and gradually diminished with milling times, due to the occurrence of nanocrystallization and reactions with ammonia. After ball milling of 7 h, the XRD peaks of CeH₂ were hardly observed. However, there were no additional diffraction peaks which suggested new phases or products resulting from ball milling of CeH₂ and NH₃. Although cerium amide was most likely formed upon ball milling, regrettably, the formation of cerium amide was not confirmed by XRD, probably due to it being nanostructured or amorphous.

However, the sample obtained after ball milling of CeH₂ and NH₃ was found to be converted into cerium nitride when subjected to thermal treatment around 873 K as described in the next section. This indicates that the reaction product of CeH₂/NH₃ is certainly cerium amide or an amide-like compound, which decomposes to CeN as described later in XRD and TPD results. Upon ball milling of CeH₂ in an atmosphere of NH₃, thus cerium hydride readily reacts with ammonia, resulting in the formation of the nanostructured cerium amide as shown in eq. (1).

\[
\text{CeH}_2 + \text{NH}_3 \rightarrow \text{Ce(NH}_2)_2 + 2\text{H}_2 \quad (1)
\]

3.2 Thermal decomposition of cerium amide to cerium nitride

Next the conversion of cerium amide to the cerium nitride was followed by taking XRD spectra with increasing in temperatures for the pretreatment. As shown by changes in XRD (Fig. 2) for CeH₂/NH₃ ball-milled for 7 h, the conversion started at about 673 K and the diffraction peaks of cerium nitride (CeN) were clearly observed upon the thermal treatment above 873 K. This indicates that the reaction of CeH₂ with NH₃ certainly occurs to form amide or amide-like products as a precursor of cerium nitride. It has been shown in previous studies that the reaction of cerium hydride (CeHₓ) with ammonia at 623 K exclusively yields cerium nitride as evidenced by XRD; even if the cerium amide is temporarily formed in this case, it is not observed due to rapid decomposition to nitride at elevated temperatures around 623 K. It was found that upon treatment at higher temperatures considerable crystallization of CeN proceeded further.

![Figure 2. Changes in XRD of (a) 7-hour milling products of CeH₂ and NH₃ with the thermal treatment. The products were subjected to evacuation for 1 h at the following temperatures: (b) 673 K, (c) 873 K and (d) 1073 K.](image)

To evaluate the processes of the conversion into CeN, TPD of the CeH₂/NH₃ products was studied (Fig. 3). The TPD traces (Fig. 3(c)) of the product after 7-hour milling of CeH₂ and NH₃ showed a broad desorption peak of NH₃ around 400 K, two desorption peaks of H₂ at temperatures around 430 and 500 K and small desorption of N₂ at 880 K. Taking into account the conversion processes of ytterbium and europium amide, Yb(NH₂)₂ and Eu(NH₂)₂, to the nitrides, YbN and EuN, the change of cerium amide to nitride are considered as follows. Cerium amide, Ce(NH₂)₂, decomposes to form the imide, CeNH, with the evolution of NH₃ according to eq. (2) and subsequently the conversion into the nitride, CeN, accompanying the evolution of H₂ occurs as shown in eq. (3).


© 2010 NWT-Verlag, Bornheim, Germany
Ce(NH$_2$)$_2$ $\rightarrow$ CeNH + NH$_3$ (2)

CeNH $\rightarrow$ CeN + 1/2H$_2$ (3)

The amide is usually converted into nitride through imide;\textsuperscript{13, 14, 15} Thus the thermal decomposition from the amide to the nitride successively occurs. However, the formation of CeNH was not confirmed in XRD studies (Fig. 2). In the decomposition reaction of rare earth amides, the formation of imide intermediates often has not been recognized. Juza et al.\textsuperscript{15} report that there is no evidence of imide formation in the conversion process of Eu(NH$_2$)$_2$ to EuN. However, TPD results obtained here were consistent with the conversion of cerium amide into nitride expressed by eqs. (2) and (3).

The evolution of N$_2$ observed around 880 K is probably due to further decomposition of CeN to CeN$_{1-x}$.

CeN $\rightarrow$ CeN$_{1-x}$ + x/2N$_2$ (4)

By the way, TPD of CeH$_2$ itself as a starting material showed two desorption peaks of hydrogen around 500 and 980 K as shown in Fig. 3(a). In the structural properties of cerium hydrides, the hydrogen atoms are distributed in the tetrahedral and octahedral sites of the fluorite-type structure and usually the tetrahedral sites are preferentially occupied in CeH$_2$ dihydride.\textsuperscript{11, 12} It can be seen by comparison of TPD traces between CeH$_2$ (Fig. 3(a)) and ball-milled CeH$_2$/NH$_3$ (Figs. 3(b) and 3(c)) that the hydrogen in CeH$_2$ which was observed around 500 K and 980 K disappeared after ball milling of CeH$_2$ and NH$_3$ for 7 h, due to reaction with ammonia according to eq. (1). Upon initial ball milling (Fig. 3(b)), hydrogen observed around 500 and 980 K started to disappear,

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{TPD for (a) CeH$_2$ as a starting material, (b) products after ball milling of CeH$_2$ and NH$_3$ for 15 min, and (c) products after ball milling of CeH$_2$ and NH$_3$ for 7 h.}
\end{figure}

\textsuperscript{13} K. Howell, L. L. Pytlewski, J. Less-Common Met. 1969, 19, 399.
\textsuperscript{14} S. Salot, J. C. Warf, J. Am. Chem. Soc. 1968, 90, 1932.
\textsuperscript{15} R. Juza, C. Hadendeldt, Naturwissenschaften 1968, 55, 229.

© 2010 NWT-Verlag, Bornheim, Germany
while newly desorbed hydrogen from the reaction products of CeH$_2$/NH$_3$ was observed around 450 K. The hydrogen of CeH$_2$ observed around 980 K completely disappeared after only 15-minute milling. Taking into account the XRD results (Fig. 1), the TPD peaks of hydrogen in CeH$_2$ gradually diminished with ball milling and almost disappeared with the completion of reaction (1) by 7-hour ball milling, as shown in Fig 3(c). For the 7-hour ball-milled CeH$_2$/NH$_3$, the TPD peaks of hydrogen observed around 430 and 500 K are assigned to hydrogen arising from the decomposition of cerium imide to nitride according to eq. (2). Probably, if cerium triamide is in part formed, the following decomposition process is possible: Ce(NH$_2$)$_3$ → CeNH + H$_2$ + 1/2N$_2$ + NH$_3$. This leads to additional hydrogen desorption in the TPD traces. In TPD studies, it was proven that cerium amide thermally decomposes to form the imide, followed by the conversion to the nitride.

Thus, cerium nitride was successfully prepared by the thermal decomposition of cerium amide obtained by the reaction of cerium hydride with ammonia, compared to the preparation method using the direct reaction of the cerium metal with ammonia reported previously.$^6$

4. Conclusion

The preparation method of cerium nitride by taking advantage of the reaction of cerium hydride with ammonia has been studied extensively. Nanostructured CeN was successfully prepared by thermal decomposition of cerium amide obtained by ball milling of CeH$_2$ and NH$_3$. The formation of cerium amide as a precursor of nitride was important in the whole steps for the preparation and was strongly suggested by XRD and TPD studies. The cerium amide obtained by ball milling of CeH$_2$ and NH$_3$ for 7 h was subjected to a thermal treatment to be converted into cerium nitride. The conversion processes of cerium amide into nitride were evaluated with XRD and TPD. Consequently, the cerium amide decomposed to imide with evolution of ammonia around 400 K, followed by conversion into nitride from about 500 K with evolution of hydrogen.

Received: August 8, 2009.
Theoretical Description of the Energy Transfer in Lanthanide Materials

Andrzej Kedziorski\textsuperscript{a,*} and Lidia Smentek\textsuperscript{a, b}

\textsuperscript{a} Institute of Physics, Nicolaus Copernicus University, ul. Grudziadzka 5, 87-100 Torun, Poland
\textsuperscript{b} Department of Chemistry, Vanderbilt University, 7330 Stevenson Center, Station B 351822, Nashville, Tennessee 37235, USA
* E-mail: tecumseh@fizyka.umk.pl

Abstract. The magnitude of the quantum yield of the sensitized luminescence of the lanthanide-organic chelates is the result of the competition between all the photophysical processes that occur in the system. The energy transfer between the ligand/antenna and the central ion plays the crucial role in the spectroscopic properties of the considered systems. Indeed, this process enables the emission from the lanthanide ion. As a consequence, the efficiency of the energy transfer is one of the leading factors that determines the quantum yield of the sensitized luminescence. Therefore, the knowledge of the efficiency of the energy transfer is crucial for designing effective luminescent lanthanide-organic chelates. The present work is devoted to the calculation of the energy transfer rate that consists of two parts, namely the matrix element of the operator, which describes the interaction between the central ion and antenna, and the spectral overlap integral. The matrix element is expressed in the terms of the effective operators by means of the Racah Algebra with the inclusion of the perturbing influence of the crystal field potential and electron correlation effects\textsuperscript{1}. This part of the energy transfer rate allows one to perform ab initio type calculations when the perturbed function approach is applied. This theoretical model is also formulated in the relativistic version\textsuperscript{2}, which is in addition to the possibility of taking into account the exchange interactions if the wave functions of the whole system (lanthanide ion and ligands) are totally antisymmetrized\textsuperscript{3}. The dependence of the energy transfer rate (and consequently, of the quantum yield of the sensitized luminescence) on factors that determine the magnitude of the overlapping of the spectral bands of the ligand/antenna and the lanthanide ion is also considered\textsuperscript{4}. As for example, the results of numerical calculations performed for Tb\textsuperscript{3+} and Yb\textsuperscript{3+} complexes are analyzed and compared to the experimentally observed correlation between the quantum yield of the sensitized luminescence of the lanthanide complexes and the position of the lowest triplet energy level of the ligand/antenna\textsuperscript{5}.

Keywords: Lanthanides; Theory; Organometallics; Spectroscopy

Introduction

The atomic-like spectra of the lanthanide materials make these systems attractive for applications in various branches of technology and medicine. The observed narrow spectral lines originate from the transitions between the states of the ground configuration 4f\textsuperscript{N} of the lanthanide ion. The majority of these so-called f-f transitions are of the electric dipole character. Thus, they are parity forbidden due to Laporte selection rule. Consequently, the f-f transition are relatively weak that very often makes the direct

\textsuperscript{1} L. Smentek, B. A. Hess, Jr., \textit{J. Alloys Compd.}, \textbf{2000}, 300-301, 165.
excitation of the lanthanide ions via the incident light ineffective. Thus, in order to obtain the highly efficient luminescence from the lanthanide material one has to excite the rare earth ion indirectly. It can be realized via the so-called sensitized luminescence in which the incident light is absorbed by the host material or the other impurity. Then the lanthanide ion is excited via the energy transfer and finally the luminescence from the lanthanide ion is observed. These sequences of the photophysical processes are called the host-sensitized or impurity-sensitized luminescence, respectively. It is seen that the energy transfer enables the sensitized luminescence and the magnitude of the energy transfer rate is one of the crucial factors that determine the quantum yield of the emission of light from the lanthanide ions. Thus, the successful design of the highly luminescent lanthanide materials has to be based on the knowledge of the efficiency of the energy transfer that occurs between the donor (host/impurity) and the acceptor (lanthanide ion). Consequently, such design needs reliable theoretical model of the energy transfer process. The classical papers of Förster\textsuperscript{6} and Dexter\textsuperscript{7, 8, 9, 10} are the first attempts to describe the energy transfer process within the framework of quantum mechanics. The energy transfer rate between the donor (D) and acceptor (A) is of the following form

$$P_{D \rightarrow A} = \frac{2\pi}{\eta} \left| \langle \Phi_f^D \Psi_f^A | V | \Phi_i^D \Psi_i^A \rangle \right|^2 F_{DA}, \quad (1)$$

where the potential $V$ defines the interaction between distinct subsystems, the donor and the acceptor, respectively. The separation of these subsystems is manifested in Eq. (1) by the simple product form of the initial ($\Phi_i^D \Psi_i^A$) and final ($\Phi_f^D \Psi_f^A$) states of the whole system. The integral $F_{DA}$ is determined by the overlapping between the emission spectrum of the donor and the absorption spectrum of the acceptor.

The possible mechanisms of the energy transfer originate from the electrostatic, magnetic and electromagnetic interaction between the donor and the acceptor. However, it was estimated in the case of allowed transitions in the subsystems that the electrostatic interaction provides the dominating contribution to the rate of the energy transfer and the remaining contribution are of negligible importance\textsuperscript{11}. The matrix element of the electrostatic potential expanded in series of interactions between consecutive multipoles $D_q^{(k)} = r^k C_q^{(k)} (\theta, \phi)$ localized on the donor ($D_i^{(m)}$) and acceptor ($D_q^{(k)}$) calculated between the product states is of the following form\textsuperscript{12}

$$\langle \Phi_f^D \Psi_f^A | V | \Phi_i^D \Psi_i^A \rangle = \sum_{m \mu} \sum_{kq} \sum_{k, m, k + m} [k, m, k + m]^{1/2} (4\pi)^{-3/2} \frac{r^{(k+m)}(\Theta, \Phi)}{R^{k+m+1}} B_{km}^{q\mu} \langle \Phi_f^D | D_i^{(m)} | \Phi_i^D \rangle \langle \Psi_f^A | D_q^{(k)} | \Psi_i^A \rangle. \quad (2)$$

The spherical coordinates $R, \Theta, \Phi$ describe the position of the donor with respect to the acceptor. The explicit form of the factor $B_{km}^{q\mu}$ can be found in Ref. 13. The electrostatic model leads to the famous Dexter’s formula for the energy transfer rate\textsuperscript{5, 11}

$$P_{D \rightarrow A} = \frac{T_e}{R^6} + \frac{T_6}{R^8} + \frac{T_8}{R^{10}} + \ldots, \quad (3)$$

where the first three terms correspond to the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole (and dipole-octupole) interactions between the donor and acceptor, respectively. These are the terms of Eq. (2) for \( m+k \) equal to 2, 3 and 4, respectively. The quantities \( T_6, T_8 \) and \( T_{10} \) can be treated as adjustable parameters that are determined within semi-empirical approach. However, only the theoretical analysis based on the results of the ab initio calculations can provide the reliable information about the importance of various terms from the Eq. (3) that contribute to the energy transfer rate. Within the latter approach one has to perform the ab initio calculations of the appropriate matrix elements of the multipole moments \( D^{(m)}_\mu \) and \( D^{(k)}_\nu \) from the Eq. (2). The theoretical model of the calculation of the matrix element of the dipole localized on the lanthanide ion is presented in the next section. The calculations of the matrix element localized on the antenna are planned for the future.

**Matrix element localized on the lanthanide ion**

The theoretical model of the calculation of the matrix element

\[
\left\langle \Psi_f^A \middle| D^{(k)}_\nu \middle| \Psi_i^A \right\rangle \tag{4}
\]

of the multipole moment localized on the lanthanide ion (the acceptor) was worked out by Smentek et al.\(^{1,2,12,14,15}\). It is based on the double perturbation approach performed for the following Hamiltonian\(^1\)

\[
H = H_0 + \lambda V_{CF} + \mu V_{\text{corr}}. \tag{5}
\]

where the zeroth-order Hamiltonian \( H_0 \) is the following

\[
H_0 = h_0 + \text{POP}, \tag{6}
\]

where \( h_0 \) is defined within the free ion approximation and the single configuration approximation; in practical realizations \( h_0 \) is usually defined within Hartree-Fock model. The operator \( P \) projects onto the space spanned by the states of \( 4f^N \) configuration, the so-called model space, and the operator \( O \) stands for all the physical effects that have to be taken into account in order to properly describe the lanthanide system. The inclusion of the perturbative effect of the crystal field potential \( V_{CF} \) and the electron correlation \( V_{\text{corr}} \) in Eq. (5) leads the description of the lanthanide system beyond the free ion and the single configuration approximations, respectively. It should be pointed out that the perturbations are defined in a following way\(^1\)

\[
V' = PVQ + QVQ + QVP, \tag{7}
\]

\[
V_{CF} = \sum_{\nu,p} B'_{\nu,p} \sum_{i=1}^N \theta_i \phi_i C^{(i)}_\nu, \tag{8}
\]

and

\[
V_{\text{corr}} = \sum_{\kappa} \sum_{l=1}^N \sum_{\rho} \left\langle \gamma_l^{(\rho)} | C^{(\kappa)}_\rho \right\rangle \left\langle C^{(\kappa)}_\rho | \gamma_l \right\rangle \sum_{l=1}^N \mathcal{E}^{(l)} \left( \gamma_l \right) C^{(l)} \tag{9}
\]


The form of the first-order contribution to the energy transfer amplitude is the matrix element of the multi-pole moment that is evaluated between the states of the ground configuration 4f^N of the lanthanide ion. In this case, the order \(k\) of the multi-pole moment has to be even due to parity requirements. The first-order contribution can be calculated directly, whereas the evaluation of the higher-order contributions to energy transfer amplitude from Eq. (11) requires the introduction of the effective operators that represent these contributions in an *effective* way. The formulation of such operators is performed within the same approach as that of the Judd-Ofelt theory of the electric dipole f-f transitions. The form of the effective operators that represent the second- and the third-order contributions to the energy transfer amplitude from Eq. (11) are presented in Ref. 12.

The general form of these effective operators can be expressed as the sum of one- and two-particle operators that act within orbital space, namely

\[
\sum_{x_3, y_3} \left[ \sum_{x, y} \lambda_3^{x,y} \right],
\]

where \(U^{(1)}(4f,4f) = \sum_{x} u^{(1)}_{x} \delta(\mathbf{n}_1, \mathbf{n}_1)\delta(\mathbf{n}_2, \mathbf{n}_2)\) and \(U^{(yA)}(4f,4f) = \sum_{x} u^{(yA)}_{x} \delta(\mathbf{n}_1, \mathbf{n}_1)\delta(\mathbf{n}_2, \mathbf{n}_2)\). All terms presented in Eq. (11) contribute to the one-particle effective operator, whereas only the second- and third-order contributions that originate from the Coulomb interaction between electrons from \(\text{corr}\) defined in Eq. (9) give rise to two-particle effective operators. The quantities \(1^{A}\) and \(2^{yA}\) consist of the radial and angular part of the effective operators. The application of the perturbed-function approach in the evaluation of the radial part of the effective operators enables the ab initio analysis of the contributions from Eq. (11). The bottle-neck of the direct calculations of the energy transfer amplitude is the presence of the structural parameters \(B_{p}\) in the quantities \(1^{A}\) and \(2^{yA}\). Namely, the lack of the reliable model of the crystal field potential prevents the
evaluation of the odd rank crystal field parameters that can be neither obtained within semi-empirical approach.

**Impact of exchange effects on the energy transfer rate**

The total wavefunction of a many electron system has to be antisymmetric with respect to permutations of all electron positions. In the model presented here the donor and acceptor are considered as independent subsystems, and as a consequence the wavefunction is a simple product of functions describing each part separately, as in Eq. (1). Each of the functions $\Phi_i^D$ and $\Psi_i^A$, for example, are antisymmetric within a distinct group of electrons of D and A, separately. However, if the donor and acceptor are treated as a whole system, the total wavefunction has to be also antisymmetric with respect to the interchange of the electrons between the subgroups. Therefore, in such cases, when the electrostatic interaction in Eq. (1) is taken into account, in addition to the direct terms defined in Eq. (2), the amplitude of the energy transfer is also determined by the exchange terms. The two-center nature of the integrals that arise in the exchange contributions to the energy transfer amplitude demands the transformation of, for example, wavefunction localized on the ligand (donor) to the reference frame of the lanthanide ion (acceptor). Smentek\(^3\) has presented the explicit treatment of the calculation of the two-center exchange integrals in the case of the energy transfer in lanthanide materials. The analysis is performed within free-ion approximation, and the impact of the crystal field potential upon the energy transfer amplitude is taken into account at the second order. It is shown that both, the first- and the second-order exchange contributions to the energy transfer amplitude are represented by the effective double tensor operators $W^{(k_1\kappa_2)}$, that act within spin and orbital spaces. This is the consequence of the application of the so-called Dirac’s identity for the permutation operator\(^3\). It should be pointed out that the effective double tensor operators in natural way also appear within the relativistic version of the theory of the energy transfer\(^2\). This means that within the semi-empirical approach, in which the parametrization scheme of the energy transfer amplitude is expressed by the double tensor operators, namely\(^3\)

$$
\sum_\lambda \sum_\kappa \Omega_{\lambda A}^D \Psi_f^A W^{(\kappa_1\kappa_2)} \Psi_i^A , \quad (13)
$$

both, the exchange terms and the relativistic effects are taken into account. It should be pointed out that the one-particle part of the direct terms considered in previous section is also included in Eq. (13) via the $\kappa = 0$ terms.

**Spectral overlap integral**

The one of the remaining factors that determines the energy transfer rate is the spectral overlap integral. It is defined in the following way\(^4,10,11,19\)

$$
F_{DA} = \int g_D(E) g_A(E) \, dE , \quad (14)
$$

where $g_D(E)$ and $g_A(E)$ are the normalized spectral bands of the donor (emission) and acceptor (absorption), respectively. Following Malta\(^9\), the spectral overlap integral in the case of the energy transfer that occurs in lanthanide complexes can be expressed as follows

\(^{19}\) O. L. Malta, J. Lumin., 1997, 71, 229-236.
where $\Delta = E_{\text{Ligand}} - E_{\text{Lanthanide}}$ is the energy distance between the band peaks of the emission band of the ligand/antenna and the absorption line of the lanthanide ion; $\Gamma_L$ is the width of the ligand emission band. It should be pointed out that the spectral overlap integral from Eq. (15) is defined for the positive values of $\Delta$. The generalization to all values of energy difference $\Delta$ can be performed by the multiplication of the Eq. (15) by the appropriate Boltzmann factor as follows\textsuperscript{4,19}

\[ F_{\text{ET}}(\Delta, \Gamma_L, T) = F_{\text{DA}}(\Delta, \Gamma_L) \exp \left( -\frac{\varepsilon|\Delta|}{k_B T} \right), \quad (16) \]

where

\[ \varepsilon = \begin{cases} 0, & \Delta \geq 0 \\ 1, & \Delta < 0 \end{cases}. \quad (17) \]

It is emphasized that Eq. (16) defines the spectral overlap integral for energy transfer form ligand/antenna to lanthanide ion. The counterpart for the back transfer from to lanthanide ion the ligand/antenna is the following\textsuperscript{4}

\[ F_{\text{BT}}(\Delta, \Gamma_L, T) = F_{\text{DA}}(\Delta, \Gamma_L) \exp \left( -\frac{(1-\varepsilon)|\Delta|}{k_B T} \right). \quad (18) \]

The analysis of the quantum yield of the sensitized luminescence of the lanthanide complexes from the point of view of its dependence on the physical factors that determine the spectral overlap integrals defined in Eqs (16) and (18) is presented in Ref. 4. In this case the lanthanide ion is considered for simplicity as the two-level system. The energy level scheme of this system is presented in the Figure 1., where the ligand/antenna is represented by the Jabłoński diagram and the possible photophysical processes are also shown in this figure.

![Figure 1. Energy level scheme of the ligand/antenna-lanthanide ion system. Photophysical processes: Abs – Absorption, Fl – Fluorescence, IC – Internal Crossing, ISC – Inter-System Crossing, Ph – Phosphorescence, ET – Energy Transfer, BT – Back Transfer, Em – Emission, NR – Non-Radiative relaxation](image)

The rate equations for this system can be written in a standard way\textsuperscript{4,20}. The evaluation of the normalized populations ($n_{00}$, $n_{01}$, $n_T$, $n_1$ and $n_2$) of the energy states of the ligand and lanthanide ion in the stationary case reduces to the problem of solution of the non-linear equations [4]. Now one is in position to calculate the quantum yield of the sensitized luminescence\textsuperscript{4,20}

\[ \phi = \frac{k_{Em} n_2}{k_{Abs} n_{S0}} , \quad (19) \]

the efficiencies of the energy transfer and the back transfer

\[ \eta_{ET} = \frac{P_{ET} n_1 n_1}{k_{ISC1} n_{S1} + P_{BT} n_{S0} n_2} \quad (20) \]

and

\[ \eta_{BT} = \frac{P_{BT} n_{S0}}{k_{Em} + k_{nr} + P_{BT} n_{S0}} , \quad (21) \]

respectively.

The illustration of the numerical results is presented in the Figure 2, where the quantum yield \( \phi \) and efficiencies of the transfer processes, \( \eta_{ET} \) and \( \eta_{BT} \), are plotted as the functions of the energy difference \( \Delta \).

---

**Figure 2.** Quantum yield of the sensitized luminescence \( (\phi) \), energy transfer and back transfer efficiencies \( (\eta_{ET} \) and \( \eta_{BT} \), respectively) calculated for the stationary state of the model systems containing Yb\(^{3+}\) or Tb\(^{3+}\) ions. Rates of the photophysical processes: \( k_{Abs} = 1 s^{-1} \), \( k_{Fl} + k_{IC} = 5 \times 10^7 s^{-1} \), \( k_{ISC1} = 5 \times 10^7 s^{-1} \), \( k_{Ph} + k_{ISC2} = 10^5 s^{-1} \), \( P_{ET} = 10^{11} \times F_{ET} s^{-1} \), \( P_{BT} = 10^{11} \times F_{BT} s^{-1} \left( \Gamma_L = 2500 cm^{-1} , T = 300K \right) \), \( k_{Em} = 10^5 s^{-1} \), \( k_{nr} = 9 \times 10^5 s^{-1} \)

\( \left( \text{Yb}^{3+} \right) \), \( k_{Em} = 1.1 \times 10^3 s^{-1} \), \( k_{NR} = 2.34 \times 10^3 s^{-1} \) \( \left( \text{Tb}^{3+} \right) \).

It should be pointed out that the values of rates of the photophysical processes that occur in ligand/antenna and the energy transfer/back transfer rates are taken to be the same in the calculations for both, the Yb\(^{3+}\) and Tb\(^{3+}\) systems. Thus, the only difference in the analysis of the sensitized luminescence of these systems is the values of the rates that determine the lifetime of the excited state of lanthanide ion. It is seen in the Figure 2 that the efficiency of the energy transfer \( \eta_{ET} \) is in practice the same for both model systems. At the same time the \( \eta_{BT} \left( \text{Yb}^{3+} \right) \) and \( \eta_{BT} \left( \text{Tb}^{3+} \right) \) efficiencies differ from each other substantially for \( \Delta > 0 \). Their behaviour can be explained in the light of the Eqs (18) and (21), which are the definitions of \( P_{BT} \) and \( \eta_{BT} \),
respectively. It is seen from Eq. (18) that the back transfer rate $P_{BT}$ is a fast-decreasing function of the positive energy difference $\Delta$. Since, for the appropriately large (positive) value of $\Delta$ the sum of rates $k_{Em} + k_{nr}$ starts to dominate over the $P_{BT}$ ($n_{S0} = 1$) in the denominator of the Eq. (21). As a consequence, the efficiency of the back transfer $\eta_{BT}$ is fast-decreasing function for $\Delta$ greater than 1000 and 2000 cm$^{-1}$ in the case of Yb$^{3+}$ and Tb$^{3+}$ systems, respectively. As was mentioned above, this is direct result of the difference in magnitude of the lifetimes of the excited states of Yb$^{3+}$ ($\sim$1 $\mu$s) and Tb$^{3+}$ ($\sim$1 ms) complexes.

![Figure 3](image_url)

**Figure 3.** Ratio of the quantum yield $\phi$ of the sensitized luminescence to the energy transfer efficiency $\eta_{ET}$ in the case of Yb$^{3+}$ and Tb$^{3+}$ complexes.

Furthermore, it should be pointed out that this theoretical result is in agreement with the experimental observation$^5$ that the back transfer in Tb$^{3+}$ complexes is completely excluded at the room temperature if $\Delta$ is greater than $10k_BT$ ($\approx$ 2000 cm$^{-1}$). Finally, the most important parameter in present analysis, the quantum yield of the sensitized luminescence $\phi$ of the considered systems, is also plotted in the Figure 2. It is seen that the luminescence is effectively quenched by the back transfer for the values of $\Delta$ smaller than 1000 and 2000 cm$^{-1}$ for Yb$^{3+}$ and Tb$^{3+}$ complexes, respectively. At the same time for the range of the values of $\Delta$ for which back transfer is negligible, the quantum yield $\phi$ seems to be proportional to the efficiency of the energy transfer $\eta_{ET}$. This can be verified by the examination of their ratio, which is presented in the Figure 3. It is seen that for appropriately large values of $\Delta$ this ratio is practically constant. This confirms the fact that if the back transfer is negligible, then the quantum yield is proportional to efficiency of the energy transfer and with this assumption, following Parker et al.$^{21}$, one can write the formula for quantum yield

$$\phi_0 = \phi_T \eta_{ET} \phi_{Em},$$  \hspace{1cm} (22)

The definition of $\phi_0$ is in fact the probability of the sequence of the three processes, the occupation of the triplet state after the excitation of ligand via the absorption of the photon ($\phi_T$), the energy transfer from ligand to lanthanide ion ($\eta_{ET}$) and emission from lanthanide ion ($\phi_{Em}$). The form of simple product of three probabilities in Eq. (22) indicates that the considered processes are independent from each other, which is correct in the limit $P_{BT} \to 0$. Furthermore, taking the definitions of $\eta_{ET}$ (Eq. (20)), $\phi_T$ and $\phi_{Em}$, namely

\[ \phi_T = \frac{k_{ISC} n_{S1}}{k_{Alb} n_{SO}} \quad (23) \]

and

\[ \phi_{Em} = \frac{k_{Em}}{k_{Em} + k_{nr} + P_{BT} n_{SO}}, \quad (24) \]

respectively, one can show that \( \phi_0 \) is the limit case of \( \phi \) for \( P_{BT} \rightarrow 0 \). On the other hand, the quantum yield \( \phi \) defined in Eq. (19) is the probability of the much more general sequence of processes than that of \( \phi_0 \), namely it covers the arbitral number of the sequences of the back transfer followed by energy transfer processeses, which is eventualy followed by the emission from lanthanide ion. It can be shown that the probability of such (infinite, in general) number of sequences of processes can be obtained just by the multiplying the \( \phi_0 \) from Eq. (28) by the convergent \( (1 < \eta_{BT} \eta_{ET} < 1) \) infinite sum

\[ \phi_0 \sum_{k=0}^{\infty} (\eta_{BT} \eta_{ET})^k. \quad (25) \]

Obviously, the above probability is equal to \( \phi \) from Eq. (19).

Finally, it should be pointed out that the numerical analysis have shown that the trend in changes of the quantum yield of the sensitized luminescence with respect to the energy difference \( \Delta \) in the case of Tb\(^{3+}\) complexes reproduces qualitatively the experimentally obtained counterpart. It can be seen by the comparison of the \( \phi \) (Tb\(^{3+}\)) presented in the Figure 2 with the Figure 4 from Ref. 5, where the experimentally obtained quantum yield for various Tb\(^{3+}\) complexes is presented as the function of the position of the lowest triplet state of the ligand. This comparison is possible if one realize that the point \( \Delta = 0 \) in the Figure 2 corresponds to the position of the excited state \(^5D_4\) of the Tb\(^{3+}\) ion. However, it should be pointed out that in present calculations there were no attempts to reproduce the absolute value of the observed quantum yield, but only its dependence on the energy difference \( \Delta \) was analyzed.

**Summary**

In this work the theory the energy transfer in lanthanide materials is presented. The theoretical ab intio model of the calculation of the matrix element of the multipole moment localized on the lanthanide ion formulated by Smentek et al.\(^{1-3, 12, 14, 15}\) is recalled. The analysis of the quantum yield of the sensitized luminescence based on the model calculations of the spectral overlap integral proposed by Malta\(^{19}\) is performed. The connection between the various formulas for quantum yield proposed by Malta et al.\(^{20}\) and Parker et al.\(^{21}\) is shown. The ab initio calculations of the matrix element of the multipole moment localized on the ligand/antenna from Eq. (2) is under consideration.
Acknowledgments

This work is performed under grant from the Polish Ministry of Science and Higher Education (research project no N N202 187636).

Received: August 18, 2009.
Luminescence of Sm\textsuperscript{2+} Doped in BaFBr

Prodipta Pal and Hans Hagemann\textsuperscript{*}

Département de Chimie Physique, Université de Genève, 30, q. E. Ansermet, CH 1211 Genève 4, Switzerland
E-mail: Hans-Rudolf.Hagemann@unige.ch

Abstract. The luminescence of Sm\textsuperscript{2+-doped BaFBr has been measured as a function of temperature and pressure. The \textsuperscript{7}F\textsubscript{J} crystal field levels have been identified and the corresponding crystal field parameters evaluated. Temperature dependent lifetime measurements allow to locate the energy of the lowest 4f\textsuperscript{5}5d\textsuperscript{1} level. Pressure dependent measurements up to 8 GPa show linear red shifts of the \textsuperscript{5}D\textsubscript{2,1,0} levels. These shifts are about 3 times stronger than the well known ruby pressure shifts and highlight thus the potential use as pressure sensors below 8 GPa.

Keywords: Rare-Earth Elements; Samarium; Luminescence; High pressure; Crystal Field

Introduction

Alkaline earth fluorohalides (MFX) doped with Eu\textsuperscript{2+} and/or Sm\textsuperscript{2+} find many applications as X-ray or neutron detectors, pressure sensors as well as optical storage by hole burning.

In this work we study the luminescence of Sm\textsuperscript{2+} in BaFBr and related hosts as a function of pressure and temperature.

Luminescence spectra of Sm\textsuperscript{2+}

Sm\textsuperscript{2+} has a 4f\textsuperscript{6} electronic ground state configuration, but the lowest energy levels of the 4f\textsuperscript{5}5d\textsuperscript{1} configuration are in the range of the \textsuperscript{5}D\textsubscript{J} levels (see Figure 1A). At low temperatures, emissions from the \textsuperscript{5}D\textsubscript{2} and \textsuperscript{5}D\textsubscript{1} level dominate, while at high temperature, emissions from the \textsuperscript{5}D\textsubscript{0} level and a broad emission from the lowest 4f\textsuperscript{5}5d\textsuperscript{1} level are observed (Figure 1B).

Figure 1. A. Lowest energy levels of Sm\textsuperscript{2+}. B. Luminescence spectra of BaFBr:Sm\textsuperscript{2+} at 10 and 453 K.

Temperature dependent spectra allowed to identify the different transitions observed and to establish an experimental energy level scheme. The experimental positions of the \textsuperscript{7}F\textsubscript{J} levels could be calculated within about 5-8 cm\textsuperscript{-1} using the following parameters (in cm\textsuperscript{-1}): F\textsuperscript{2} = 332, \xi = 1054, B\textsuperscript{4f} = -279, B\textsuperscript{4d} = -125, B\textsuperscript{4g} = -156, B\textsuperscript{6f} = 433 and B\textsuperscript{6d} = -118. The agreement for the \textsuperscript{5}D\textsubscript{J} levels is less satisfactory, however it is likely that these levels are subject to configuration interaction with the lowest 4f\textsuperscript{5}5d\textsuperscript{1} levels.
Lifetime measurements as a function of temperature show a strong decrease of the lifetime of the \( ^5\text{D}_1 \) level which is related to a non-radiative transition to the lowest \( ^4\text{f}^8\text{s}^1 \) level. The energy separation between these two levels could be estimated to be \( 2712 \pm 29 \text{ cm}^{-1} \).

High pressure experiments were performed at room and low temperatures up to about 8 GPa. The emissions of the \( ^5\text{D}_1 \) levels are red shifted by more than 20 cm\(^{-1}\)/GPa, which is an about 3 times stronger shift than the corresponding shift of the ruby \( \text{R}_1 \) and \( \text{R}_2 \) lines.

Figure 2 illustrates the splitting of the \( ^7\text{F}_1 \) level as a function of pressure in BaFBr and SrFBr\(^1\). A systematic shift can be observed, and the values of the two host materials follow a similar trend.

**Figure 2.** Pressure dependent splitting of the \( ^7\text{F}_1 \) level in BaFBr and SrFBr.

**Experimental Section**

**Synthesis.** Small Sm\(^{3+}\)-doped BaFBr and SrFBr crystals were obtained by slow cooling of stoichiometric melts of commercial barium (strontium) fluoride and anhydrous bromide under dry nitrogen atmosphere using graphite crucibles. Samarium was added as SmF\(_3\) with a mole fraction of less than 1% respective to Ba or Sr.

**Optical measurements.** To obtain the low temperature we used a closed-cycle Oxford cryostat. High temperature spectra were obtained using a home-built furnace. Different lasers with emission wavelengths of 405 nm, 488 nm and 532 nm were used as excitation sources. Luminescence spectra were obtained using a Bruker IFS66 FT instrument. Lifetime measurements were performed using a SR 430 Multichannel Scaler and a Spex 270 Monochromator. A D’Anvils Diamond Anvil Cell (DAC) with a 4:1 methanol:ethanol mixture as pressure transmitting medium was used to generate high pressure. The pressure was monitored using the ruby (present with the sample) luminescence.

**Crystal field calculations.** The crystal field parameters were estimated using the program by Edvardsson and Aberg\(^2\) which calculates all energy levels of the \( 4f^n \) configuration. As only \( ^5\text{D}_1 \) and \( ^7\text{F}_1 \) levels are observed for Sm\(^{3+}\), the adjustable free ion parameters were limited to \( F_2 \) (\( F_4 \) and \( F_6 \) are related to \( F_2 \)) and the spin-orbit coupling parameter \( \xi \). Using an iterative routine written by D. Lovy of our department, selected parameters can be optimized by comparison with experimental data.

**Acknowledgements.**

This work has been supported by the Swiss National Science Foundation. The authors thank D. Lovy for implementing the crystal field calculation programs.

Received: August 19, 2009.

---


Synthesis and Characterization of an Imidazolin-2-iminato Yttrium Complex with an Exceptionally Short Metal-Nitrogen Bond

Matthias Tamm,* Alexandra G. Trambitas, Cristian Hrib, Peter G. Jones

Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina, Hagenring 30, D-38106 Braunschweig, Germany

E-mail: m.tamm@tu-bs.de

Abstract. The reaction of 1,3-di-tert-butylimidazolin-2-imine (Im$^\text{thi}$NH, 1-H) with trimethylsilylmethyl lithium (LiCH$_3$SiMe$_3$) and anhydrous yttrium trichloride (YCl$_3$) afforded the imidazolin-2-iminato complex [(1)YCl$_2$(THF)$_3$] (2). X-ray crystal structure determination revealed the presence of an unusually short yttrium-nitrogen bond of 2.115(2) Å, which represents the shortest reported for yttrium complexes to date.

Keywords: Rare-Earth Elements; Imido Ligands; N-Heterocyclic Carbenes; Yttrium

Introduction

Organoimido complexes of the transition metals have been extensively studied because of their important role in a number of biological, industrial and catalytic processes.$^1$ In stark contrast to the large number of imido complexes containing d-block elements, the imido chemistry of the f-elements is much less developed, and reports on well-defined lanthanide imido complexes are scarce.$^2$ More specifically, structurally characterized lanthanide complexes containing terminal imido groups are unknown to date, since the imido group is generally found to bind in a capping or bridging fashion. The situation is similar in organo-group 3 metal chemistry$^3$ despite several efforts to isolate terminal scandium imido complexes.$^4$ Only recently, however, evidence has been presented for the existence of a transient Sc=NR species.$^5$

Coordination of the formally dianionic imido ligand (NR)$^2$ as a terminal ligand involves a metal-nitrogen multiple bond consisting of one σ and either one or two π interactions.$^7$ This resembles the bonding in transition metal complexes containing monoanionic imidazolin-2-iminato ligands such as Im$^\text{thi}$N (1), which can be described by the two limiting resonance structures 1A and 1B (Scheme 1), indicating that the ability of the imidazolin ring to stabilize a positive charge leads to highly basic ligands with a strong electron donating capacity towards early transition metals.$^8$ Because of their ability to act as 2σ,4π-electron donors, these ligands...

---

$^3$ H. S. Chan, H. W. Li, Z. Xie, Chem. Commun. 2002, 652; the dinuclear ytterbium complex {[(dippN)Yb-(µ-Ndipp)]$_2$}$_2$ reported in this reference could be regarded as a lanthanide complex containing terminal 2,6-diisopropylphenylimido ligands (DippN), if the bridging lithium and sodium cations are ignored.
can be regarded as monodentate analogues of cyclopentadienyls, C₅R₅, and also as monoanionic imido ligands in a similar fashion to that described for related phosphoraneiminato ligands. Therefore, lanthanide complexes with terminal imidazolin-2-iminato ligands might serve as models for elusive mononuclear lanthanide imido complexes, and their structural investigation could lead to a better understanding of lanthanide-nitrogen multiple bonding. Recently, we have reported the preparation and structural characterization of several scandium, yttrium, gadolinium and lutetium complexes containing the 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-iminato ligand (ImDippN); these complexes feature very short metal-nitrogen bonds, which are among the shortest ever observed for these elements. Since the substituents on the imidazole heterocycle can easily be varied, numerous imidazolin-2-iminato ligands are available, and in this contribution, the preparation and structural characterization of the yttrium complex [(1)YCl₂(THF)₃] (2) is reported, which represents the first rare-earth metal complex containing the 1,3-di-tert-butylimidazolin-2-iminato ligand ImtBuN (1).

Results and Discussion

The reaction of the imine 1-H with trimethylsilylmethyl lithium (Me₃SiCH₂Li) and anhydrous yttrium trichloride in THF solution afforded the imidazolin-2-iminato complex [(1)YCl₂(THF)₃] (2) as a colourless crystalline solid in good yield after extraction with pentane and crystallization from THF/pentane solution (1:2) (Scheme 2). 2 was fully characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. Coordination to the rare earth metal does not have a significant impact on the resonances observed for the hydrogen and carbon atoms of the heterocyclic imidazoline moiety; the ¹H NMR spectrum at room temperature exhibits two singlet resonances at 6.05 and 1.55 ppm for the imidazole CH and CH₃ groups, respectively.

The molecular structure of 2 was also established by X-ray diffraction analysis; 2 crystallizes in the orthorhombic space group Pbcn with crystallographic twofold symmetry (the twofold axis is horizontal in Scheme 2 and Figure 1). The axial THF ligand is disordered about the twofold axis. The overall structural parameters are very similar to those previously reported for the related complexes [(ImDippN)MCl₂(THF)₃] (M = Sc, Y, Gd, Lu); and the molecular structure is shown in Figure 1. The metal atom is hexacoordinated with the two chlorine atoms in trans-position and the three THF ligands adopting a meridional arrangement. The Cl-Y-Cl* (155.92(3)°) and O1-Y-O1* (170.65(6)°) angles deviate significantly from 180°, whereas the N1-Y-O2 and C1-N1-Y angles are exactly 180° by symmetry. Thus, the coordination geometry about the metal atom can be described as a distorted octahedron or, since the Y-O2 bond (2.458(2) Å) is considerably longer than the other two Y-O bonds (2.3262(14) Å), this THF ligand can be regarded as being trans-coordinated to a square-pyramid...
with the imido N1 atom at the apex. Presumably, the elongation of the Y-O2 bond is a result of the strong N1-Y interactions, revealed by a very short Y-N1 bond length of 2.115 Å. This value is even slightly smaller than observed for the corresponding ImDippN complex (2.1278(18) Å);\(^\text{12}\) it is almost identical with the previously shortest yttrium-nitrogen bond of 2.116(6) Å that was observed in a tetranuclear cyclopentadienyl-yttrium complex containing µ-ethylimido ligands.\(^\text{13}\) Short Y-N distances have also been reported for yttrium-phosphoraneiminato complexes.\(^\text{14}\)

In summary, the structural characterization of complex 2 gives further evidence for the suitability of imidazolin-2-iminato ligands to form particularly strong metal-nitrogen bonds. In analogy to the chemistry involving the ImDippN ligand,\(^\text{12}\) the dihalide 2 represents a suitable starting material for the preparation of novel yttrium complexes containing the Im\(^{\text{tBu}}\)N ligand. This chemistry and also the applicability of the resulting complexes in homogeneous rare-earth metal catalysis will be further exploited.

**Figure 1:** ORTEP drawing of 2 with ellipsoids at the 50% level; selected bond lengths [Å] and angles [°]: Y-N1 2.115(2), Y-O1 2.3262(14), Y-O2 2.458(2), Y-Cl 2.6283(6), C1-N1 1.277(4); N1-Y-O1 94.68(3), N1-Y-O2 180°, O1-Y-O2 85.32(3), O1-Y-O1' 170.65(6), Cl-Y-C1' 155.92(3), Cl-Y-O2 77.959(14), Cl-Y-O2 89.69(4), C1-N1-Y 180°.

**Experimental Section**

**General.** All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10\(^{-4}\) torr) line, or in an argon-filled glove box (MBraun 200B). All solvents were purified by a solvent purification system from MBraun and stored over molecular sieve (4 Å) prior to use. Deuterated solvents were obtained from Sigma Aldrich (all ≥ 99 atom % D) and were degassed, dried, and stored in the argon-filled glove box. NMR spectra were recorded on Bruker DPX 200. The chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as internal standard (\(^1\)H, \(^{13}\)C). Elemental analysis (C, H, N) succeeded by combustion and gas chromatographical analysis with an Elementar vario MICRO. 1,3-Di-tert-butylimidazolin-2-imine (Im\(^{\text{tBu}}\)NH, 1-H)\(^a\) and [LiCH\(_2\)SiMe\(_3\)]\(^{15}\) were prepared according to published procedures. Anhydrous YCl\(_3\) was purchased from Sigma-Aldrich and used as received.

**Preparation of Complex [(I)YCl\(_2\)(THF)] (2).** A mixture of anhydrous YCl\(_3\) (300 mg, 1.53 mmol) and LiCH\(_2\)SiMe\(_3\) (144 mg, 1.53 mmol) was treated with THF (20 mL). After stirring for 12 h, a solution of 1-H (300 mg, 1.53 mmol) in THF (20 mL) was added. The reaction mixture was allowed to stir for another 12 h. The solvent was evaporated, and the compound was repeatedly extracted with 30 mL (3 x 10 mL) of toluene. The complex was recrystallized from THF/pentane (3:1) at –30°C to obtain colourless crystals.

---


\(^{15}\) G. D. Vaughn, K. A. Krein, J. A. Gladysz, *Organometalics* 1986, 5, 936

© 2010 NWT-Verlag, Bornheim, Germany
Analytical Data for [(1)YCl₂(THF)₃] (2). Yield: 356 mg (64.5%). Anal. Calcd for C₁₁H₂₀Cl₂N₃Y (2): C, 37.31; H, 5.69; N, 11.87. Found: C, 36.11; H, 5.72; N, 11.29. NMR (THF-d₈, 200 MHz, 25 °C): δ 6.05 (s, 2 H, NCH), 1.55 (s, 18 H, CH₃); ¹³C NMR (THF-d₈, 200 MHz, 25°C): δ 105.7 (NCH), 54.5 (CCH₃), 29.1 (CCH₃) ppm.; the NCN resonance was not observed.

Crystal structure of 2. Data were recorded with monochromated Mo-Kα radiation (λ = 0.71073 Å) on an Oxford Diffraction Xcalibur S diffractometer at low temperature. The structure was refined anisotropically using the program SHELXL-97.¹⁶ Hydrogen atoms were included using rigid methyl groups or riding model. Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-745165. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for [(1)YCl₂(THF)₃]: C₂₃H₄₄Cl₂N₃O₃Y, 570.42 g mol⁻¹, T = 100 K; 2θmax = 56.6°; ρcalc = 1.372 g cm⁻³; 50286 measured reflections of which 3417 were independent; Rint = 0.0540; F(000) = 1200; μ = 2.333 mm⁻¹. Orthorhombic, Pbcn, a = 913.45(2), b = 1772.53(6), c = 1705.30(6) pm, V = 2.76108(15)·nm³, Z = 4; R values: R1/wR2 for 3417 reflections with |I|>2σ|I₀|: 0.0292 / 0.0680; for all data: 0.0678 / 0.0725; S = 0.928. Highest peak 0.760 and deepest hole –0.561 e Å⁻³.

Acknowledgements.

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through the program “Lanthanoidspezifische Funktionalitäten in Molekül und Material” (SPP 1166).

Received, August 28, 2009.

Investigation of Lanthanide(III) Coordination Compounds with 4-Pentenoic and 3-Butenoic Acids

Grazyna Oczko*

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland
E-mail: go@wchuwr.pl

Abstract. The presented investigations confirm application of the spectroscopic studies as an useful way to consider the Ln – L bond nature. The parameters determined on the basis of absorption spectra and their variation point out the changes in polarity and strength Ln – L bond, what qualifies the lanthanide carboxylates as precursors of catalysts. A new type of coordination compounds of formula Ln(C_5H_7O_2)_3.2H_2O (where Ln = Pr, Nd, Eu; C_5H_7O_2 = 4-pentenoic anion (I)) and Ln(C_4H_5O_2)_3.2H_2O (where Ln = Pr, Nd, Eu, Ho, Er; C_4H_5O_2 = 3-butenoic anion (II)) were obtained in the aqueous solutions and as crystals. The surrounding of Ln^{3+} ions both in the solution and in the crystal was characterized by UV-Vis electronic spectroscopy at room and low temperatures. The parameter values determined on the basis of these spectra (eg. the nephelauxetic ratio \( \beta, R = I_{\text{vib.}}/I_{\text{0-phonon}} \) rates as quantity of vibronic coupling and others) and their variations were analysed. The correlation between the vibronic coupling and covalency is discussed. In the lanthanide series from La^{3+} to Lu^{3+} the ionic contributions to the metal – ligand bond increase less than the covalent ones and depend on the metal atomic number. This dependence is not linear. We observed the minimum for europium compounds. The relation between hypersensitivity and covalency is also discussed.

Keywords: Lanthanide; Carboxylates; Spectroscopy

Introduction

The great interest in the systematic investigation of open–framework structures constructed from monocarboxylate units is mainly due to their potential practical applications. These kinds of materials possess channels and other features that make them porous, which can impart potential catalytic properties\(^1\). The metal carboxylates are, too, interesting by reason of the fact that the carboxylate group acts as a linker between inorganic parts of different compounds.

Lanthanide cations behave as hard Lewis acids and bind most strongly to hard bases such as oxygen. Thus, the rare earths have strong ionic bonds in complexes with O–ligating atoms. As a consequence, the strength of such bonds depend on the distribution of electron density of active metal ions, the binding site(s) of the ligand and the distance of the metal–donor atoms. The last factor is affected by steric factors related to the structural characteristics of the ligand\(^2\). As it is well known that the strength of the metal–donor atom interaction (for example bond polarity) can be changed by varying the distribution of electron density of the ligating atom, which in turn influences the activity and stereoselectivity of the catalyst\(^3\). The used spectroscopic methods and the spectral parameters determined on their base can be a good instrument to investigate the nature of the Ln^{3+}–L bond, which is very important when considering the potential applications of lanthanide carboxylates in catalysis.

The aim of the present paper is to estimate the degree of Ln^{3+}–O bond covalency. We report on spectroscopic studies of Ln(C_5H_7O_2)_3.2H_2O (where Ln = Pr, Nd, Eu; C_5H_7O_2 = 4-pentenoic anion (I)) and Ln(C_4H_5O_2)_3.2H_2O (where Ln = Pr, Nd, Eu, Ho, Er; C_4H_5O_2 = 3-butenoic anion (II)) obtained in aqueous solutions and as crystals, especially absorption, emission and emission-excitation spectra at room temperature.

down to 4.2 K. The variation of the spectroscopic parameters for the title compounds are correlated with those for the other lanthanide carboxylates. These results are used to investigate the nature of the metal–ligand bond and the distribution of the electron density of the active metal ions.

Results and Discussion

The calculated oscillator strength values (P) for the identified transitions are presented in Tables 1–5. The experimental oscillator strength values determined from the room temperature spectra are used to estimate the $\tau_2$ intensity parameters (see Tables 1, 2, 4, 5). For all lanthanide carboxylates under study several fittings of $\tau_2$ parameters were performed and the fit was optimised to minimise the root mean square (RMS) deviation, calculated as radical of the sum of squares of deviations divided by the difference of the number of considered transitions and the number of parameters. Only the results of the best fits are presented. It is worth to note that errors in the estimation of $\tau_2$ parameters are small (even for the Pr$^{3+}$ ion). Intensities of the f-f transitions at room temperature, in particular for hypersensitive transitions, are higher than those usually found for aquo-ions$^{3,5}$. We also observe this relation for the $\tau_2$ parameter values. This behaviour can be most likely attributed to the influence of the carboxylate anions, which can change the first coordination sphere of the lanthanide ions and lead to a symmetry decrease of this sphere. Our spectra measured at 4.2 K for the Nd(H$_2$C=CH-CH$_2$COO)$_3$·2H$_2$O and Ho(H$_2$C=CH-CH$_2$COO)$_3$·3H$_2$O crystals show the splitting of the Ln$^{3+}$ ion manifolds in the crystal field$^6$ which confirms that the lanthanide ions occupy low symmetry sites in the crystal structure.

An inspection of Tables 3 and 4 shows that the oscillator strength values of the 4f-4f transitions are lower at 4.2 K than at 293 K, especially for the hypersensitive transitions. The same behaviour was observed previously by us for the halogeno derivatives of rare earth acetates$^7$. It can be attributed to the electron-phonon coupling and/or depopulation of the Stark components of the ground state multiplet, and it demonstrates well the contribution of a vibronic mechanism to the intensities of the electronic transitions.

Figures 1 and 2 show the absorption spectra of Nd(H$_2$C=CH-CH$_2$COO)$_3$·2H$_2$O and Ho(H$_2$C=CH-CH$_2$COO)$_3$·3H$_2$O single crystals at 4.2 K. The band structure is very rich, i.e. the spectra consist of many narrow lines with bandwidths of several wavenumbers. The identification of the observed groups of lines can be easily achieved by a comparison with the calculated energies of the Ln$^{3+}$ aquo-ions$^{5,5}$. The 4.2 K absorption spectra of the investigated crystals show that the number of the observed Stark electronic components of the f-f transitions is rather in agreement with that expected from group theory for the one site of Ln$^{3+}$ ions$^5$. On the other hand, some additional lines with very low intensities coupled with the respective electronic lines are observed. They are most likely of vibronic origin. This behaviour is similar to that observed previously for other Ln$^{3+}$ systems$^{8,9}$. Inspection of the IR spectra of Nd(H$_2$C=CH-CH$_2$COO)$_3$·2H$_2$O and Ho(H$_2$C=CH-CH$_2$COO)$_3$·3H$_2$O single crystals (Figures 3 and 4) shows that the energy of some bands corresponds well to the weak sideband lines observed in the absorption spectra. This observation allows us to conclude that the Ln-ligand vibrations promote relatively strong vibronic lines appearing at displacement frequencies of the localised to the stretching ν(Ln-O) and lattice modes. Our results prove, therefore, the presence of vibronic coupling for the investigated compounds, which have usually rather ionic than covalent character.

According to the existing theories of the electron-phonon coupling probability, the 4f-4f transitions with $\Delta J = 0, 2, 4$ should be considered in the analysis of this vibronic coupling$^{10}$. In order to describe this phenomenon quantitatively estimated the strength of the vibronic coupling, the deconvolution into electronic and vibronic components was performed for each particular band corresponding to the 4f-4f transitions at 4.2 K using the TAUS programme$^{11}$. Then the sum of the integrated intensities for all observed vibronic side bands ($I_{\text{Vib}}$), the integrated intensity of zero-phonon electron lines ($I_{\text{0 phonon}}$) and the rates $R = I_{\text{Vib}}/I_{\text{0 phonon}}$ were calculated. The results are presented in Table 6. The parameters, determined on the basis of the absorption spectra: the nephelauxetic ratio $\beta$ and Sinha’s parameter $\delta$ can be used to investigate and to compare the nature of metal-ligand bond.

---


Table 1. The oscillator strength values $P \cdot 10^{-8}$ of f-f transitions and the $\tau \cdot 10^{-9}$ parameter values at 293 K for Pr(H$_2$C=CH-CH$_2$COO)$_3$ and Pr(H$_2$C=CH-CH$_2$COO)$_3$ solutions

<table>
<thead>
<tr>
<th></th>
<th>Pr(H$_2$C=CH-CH$_2$COO)$_3$</th>
<th>Pr(H$_2$C=CH-CH$_2$COO)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\text{H}_4$</td>
<td>-</td>
<td>152.42</td>
</tr>
<tr>
<td>$^3\text{D}_2$</td>
<td>262.67</td>
<td>318.67</td>
</tr>
<tr>
<td>$^3\text{P}_0$</td>
<td>114.16</td>
<td>213.43</td>
</tr>
<tr>
<td>$^3\text{P}_1$, $^1\text{L}_6$</td>
<td>457.06</td>
<td>641.80</td>
</tr>
<tr>
<td>$^3\text{P}_2$</td>
<td>1135.05</td>
<td>1431.23</td>
</tr>
<tr>
<td>$\tau_2 \cdot 10^9$ [cm]</td>
<td>13.55±0.63</td>
<td></td>
</tr>
<tr>
<td>$\tau_4 \cdot 10^9$ [cm]</td>
<td>0.60±0.03</td>
<td></td>
</tr>
<tr>
<td>$\tau_6 \cdot 10^9$ [cm]</td>
<td>4.54±0.04</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. The oscillator strength values $P \cdot 10^{-8}$ of f-f transitions and the $\tau \cdot 10^{-9}$ parameter values at 293 K for Nd(H$_2$C=CH-CH$_2$COO)$_3$ and Nd(H$_2$C=CH-CH$_2$COO)$_3$ solutions

<table>
<thead>
<tr>
<th></th>
<th>Nd(H$_2$C=CH-CH$_2$COO)$_3$</th>
<th>Nd(H$_2$C=CH-CH$_2$COO)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4\text{I}_{9/2}$</td>
<td>-</td>
<td>205.95</td>
</tr>
<tr>
<td>$^4\text{F}_{5/2}$</td>
<td>240.09</td>
<td>847.60</td>
</tr>
<tr>
<td>$^4\text{F}<em>{7/2}, ^2\text{H}</em>{9/2}$</td>
<td>853.37</td>
<td>852.87</td>
</tr>
<tr>
<td>$^4\text{F}_{9/2}$</td>
<td>52.75</td>
<td>58.91</td>
</tr>
<tr>
<td>$^4\text{H}_{11/2}$</td>
<td>14.49</td>
<td>16.58</td>
</tr>
<tr>
<td>$^4\text{G}<em>{5/2}, ^2\text{G}</em>{7/2}$</td>
<td>1428.16</td>
<td>1702.39</td>
</tr>
<tr>
<td>$^2\text{K}_{15/2}$</td>
<td>690.76</td>
<td>734.57</td>
</tr>
<tr>
<td>$^2\text{G}<em>{9/2}, ^2\text{F}</em>{7/2}, ^2\text{G}_{9/2}$</td>
<td>188.61</td>
<td>188.12</td>
</tr>
<tr>
<td>$^2\text{F}_{11/2}$</td>
<td>26.36</td>
<td>29.69</td>
</tr>
<tr>
<td>$^2\text{D}_{9/2}$</td>
<td>3.45</td>
<td>5.03</td>
</tr>
<tr>
<td>$^2\text{D}_{5/2}$</td>
<td>1039.64</td>
<td>906.46</td>
</tr>
<tr>
<td>$^2\text{L}_{15/2}$</td>
<td>159.31</td>
<td>52.09</td>
</tr>
<tr>
<td>$^2\text{I}<em>{13/2}, ^2\text{D}</em>{7/2}$</td>
<td>468.76</td>
<td>248.00</td>
</tr>
<tr>
<td>$\tau_2 \cdot 10^9$ [cm]</td>
<td>4.03±0.42</td>
<td>5.2±0.67</td>
</tr>
<tr>
<td>$\tau_4 \cdot 10^9$ [cm]</td>
<td>6.28±0.40</td>
<td>5.4±0.62</td>
</tr>
<tr>
<td>$\tau_6 \cdot 10^9$ [cm]</td>
<td>9.70±0.55</td>
<td>10.00±0.86</td>
</tr>
</tbody>
</table>
Table 3. The oscillator strength values $P \cdot 10^{-8}$ of f-f transitions at 293 K and 4.2 K for a Nd(H$_2$C=$\text{CH}$-$\text{CH}_2$COO)$_3$·2H$_2$O crystal

<table>
<thead>
<tr>
<th>Transition</th>
<th>Nd(H$_2$C=$\text{CH}$-$\text{CH}_2$COO)$_3$·2H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{4}I_{9/2}$ →</td>
<td></td>
</tr>
<tr>
<td>$^{4}F_{9/2}$</td>
<td>166.05</td>
</tr>
<tr>
<td>$^{4}F_{7/2}$, $^{4}H_{9/2}$</td>
<td>594.11</td>
</tr>
<tr>
<td>$^{4}F_{5/2}$, $^{4}S_{5/2}$</td>
<td>588.55</td>
</tr>
<tr>
<td>$^{4}F_{3/2}$</td>
<td>47.91</td>
</tr>
<tr>
<td>$^{2}H_{11/2}$</td>
<td>3.52</td>
</tr>
<tr>
<td>$^{4}G_{5/2}$, $^{2}G_{7/2}$</td>
<td>1393.36</td>
</tr>
<tr>
<td>$^2$K$<em>{13/2}$, $^4$G$</em>{15/2}$</td>
<td>530.61</td>
</tr>
<tr>
<td>$^2$K$<em>{11/2}$, $^2$G$</em>{13/2}$, $^2$D$<em>{5/2}$, $^4$F$</em>{11/2}$</td>
<td>76.72</td>
</tr>
<tr>
<td>$^2$P$_{1/2}$</td>
<td>28.30</td>
</tr>
<tr>
<td>$^2$D$_{5/2}$</td>
<td>14.29</td>
</tr>
<tr>
<td>$^4$D$<em>{3/2}$, $^4$D$</em>{5/2}$, $^2$I$<em>{11/2}$, $^4$I$</em>{11/2}$</td>
<td>1011.70</td>
</tr>
<tr>
<td>$^2$L$_{15/2}$</td>
<td>22.87</td>
</tr>
<tr>
<td>$^2$I$<em>{13/2}$, $^2$D$</em>{21/2}$</td>
<td>155.07</td>
</tr>
</tbody>
</table>

Table 4. The oscillator strength values $P \cdot 10^{-8}$ of f-f transitions at different temperatures and the $\tau_\lambda \cdot 10^{-9}$ parameter values at 293 K for Ho(H$_2$C=$\text{CH}$-$\text{CH}_2$COO)$_3$·3H$_2$O, $C_{\text{Ho}^{3+}} = 0.0985 \text{ mol/dm}^3$ (solution), $C_{\text{Ho}^{3+}} = 3.754 \text{ mol/dm}^3$ (crystal)

<table>
<thead>
<tr>
<th>Transition</th>
<th>293 K</th>
<th>293 K</th>
<th>4.2 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$F$_6$</td>
<td>91.78</td>
<td>79.28</td>
<td></td>
</tr>
<tr>
<td>$^3$F$_5$</td>
<td>26.35</td>
<td>17.46</td>
<td></td>
</tr>
<tr>
<td>$^3$S$_{2}$, $^3$F$_4$</td>
<td>346.72</td>
<td>144.45</td>
<td>199.86</td>
</tr>
<tr>
<td>$^3$F$_3$</td>
<td>470.65</td>
<td>216.74</td>
<td>186.61</td>
</tr>
<tr>
<td>$^3$F$_2$</td>
<td>154.12</td>
<td>83.84</td>
<td>80.15</td>
</tr>
<tr>
<td>$^3$F$_1$</td>
<td>66.03</td>
<td>36.02</td>
<td>43.04</td>
</tr>
<tr>
<td>$^3$G$_8$</td>
<td>53.30</td>
<td>20.12</td>
<td>51.07</td>
</tr>
<tr>
<td>$^3$G$_6$, $^3$I$_1$</td>
<td>1617.92</td>
<td>1526.56</td>
<td>595.04</td>
</tr>
<tr>
<td>$^3$G$_4$, $^3$G$_3$</td>
<td>295.19</td>
<td>186.92</td>
<td></td>
</tr>
<tr>
<td>$^3$G$_2$, $^3$K$_2$</td>
<td>110.61</td>
<td>43.91</td>
<td></td>
</tr>
<tr>
<td>$^3$G$<em>1$, $^3$H$<em>1$, $^3$I$</em>{11/2}$, $^3$I$</em>{7/2}$ $^3$F$^2$</td>
<td>311.27</td>
<td>38.25</td>
<td></td>
</tr>
<tr>
<td>$^3$I$<em>{15/2}$, $^3$I$</em>{13/2}$, $^3$I$<em>{11/2}$, $^3$I$</em>{9/2}$</td>
<td>22.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3$I$<em>{7/2}$, $^3$I$</em>{5/2}$</td>
<td>155.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_\lambda \cdot 10^{-9}$ [cm]</td>
<td>4.27±0.91</td>
<td>2.51±0.46</td>
<td></td>
</tr>
<tr>
<td>$\tau_\lambda \cdot 10^{-9}$ [cm]</td>
<td>5.39±0.60</td>
<td>6.14±0.30</td>
<td></td>
</tr>
<tr>
<td>$\tau_\lambda \cdot 10^{-9}$ [cm]</td>
<td>4.25±0.83</td>
<td>1.82±0.42</td>
<td></td>
</tr>
</tbody>
</table>

© 2010 NWT-Verlag, Bornheim, Germany
Table 5. The oscillator strength values $P \times 10^{-8}$ of f-f transitions at different temperatures and the $\tau \times 10^{-9}$ parameter values at 293 K for the Er(H$_2$C=CH-CH$_2$COO)$_3$ solution, $C_{Er} = 0.04125$ mol/dm$^3$.

<table>
<thead>
<tr>
<th>Transition:</th>
<th>Wavelength</th>
<th>$P \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4I_{11/2}$</td>
<td>1060-900</td>
<td>834.76</td>
</tr>
<tr>
<td>$^4I_{9/2}$</td>
<td>830-780</td>
<td>34.23</td>
</tr>
<tr>
<td>$^4F_{9/2}$</td>
<td>680-630</td>
<td>211.98</td>
</tr>
<tr>
<td>$^4S_{3/2}$</td>
<td>560-535</td>
<td>57.48</td>
</tr>
<tr>
<td>$^4H_{11/2}$</td>
<td>535-500</td>
<td>459.10</td>
</tr>
<tr>
<td>$^4F_{7/2}$</td>
<td>500-470</td>
<td>205.01</td>
</tr>
<tr>
<td>$^4F_{3/2}$</td>
<td>460-430</td>
<td>105.92</td>
</tr>
<tr>
<td>$^4F_{9/2}$</td>
<td>420-400</td>
<td>66.11</td>
</tr>
<tr>
<td>$^4G_{11/2}$</td>
<td>390-375</td>
<td>1056.67</td>
</tr>
<tr>
<td>$^4G_{9/2}$</td>
<td>375-365</td>
<td>1007.97</td>
</tr>
<tr>
<td>$^2K_{15/2}$</td>
<td>365-350</td>
<td>1232.81</td>
</tr>
</tbody>
</table>

| $\tau_2 \times 10^9$ [cm] | 2.45±6.13 |
| $\tau_4 \times 10^9$ [cm] | 6.35±9.96 |
| $\tau_6 \times 10^9$ [cm] | 5.23±6.30 |

Table 6. $I = \text{LnX}_3$, $X = 4$-pentenoic anion (H$_2$C=CH-CH$_2$-CH$_2$COO$^-$), $\text{II} = \text{LnY}_3$, $Y = 3$-butenoic anion (H$_2$C=CH-CH$_2$COO$^-$).

<table>
<thead>
<tr>
<th>$Pr^{3+}$</th>
<th>$Nd^{3+}$</th>
<th>$Er^{3+}$</th>
<th>$Ho^{3+}$</th>
<th>$Er^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I$</td>
<td>$II$</td>
<td>$I$</td>
<td>$II$</td>
<td>$I$</td>
</tr>
<tr>
<td>solution</td>
<td>solution</td>
<td>solution</td>
<td>crystal</td>
<td>solution</td>
</tr>
</tbody>
</table>

| Energy (cm$^{-1}$) of transitions: | | | | |
| $^2H_{11/2} \rightarrow ^2I_{11/2}$ (Pr) | $^4I_{15/2} \rightarrow ^2I_{11/2}$ (Nd) | $^4I_{15/2} \rightarrow ^2I_{11/2}$ (Eu) | $^4I_{15/2} \rightarrow ^2I_{11/2}$ (Er) | $^4I_{15/2} \rightarrow ^2I_{11/2}$ (Er) | |
| 20736 | 22502 | |
| 20734 | 22490 | |

| Energy (cm$^{-1}$) of hypersensitive transitions | | | | |
| $^2H_{11/2} \rightarrow ^2I_{11/2}$ (Pr) | $^4I_{15/2} \rightarrow ^2I_{11/2}$ (Nd) | $^4I_{15/2} \rightarrow ^2I_{11/2}$ (Eu) | $^4I_{15/2} \rightarrow ^2I_{11/2}$ (Er) | $^4I_{15/2} \rightarrow ^2I_{11/2}$ (Er) |
| 22502 | 22212 | 22331 |
| 22490 | 18624 | 18634 |

| $\beta$ | 0.9974 | 1.0044 | 1.0027 | 1.0057 | 1.0010 | 0.9995 | 0.9993 | 1.0030 | 1.0030 | 1.0084 |
| $\delta$ | 0.26 | 0.41 | 0.30 | 0.54 | 0.10 | 0.05 | 0.07 | 0.30 | 0.30 | 0.83 |

$R = I_{1b}/I_{2b\text{photon}}$ | 0.30 | 0.30 | 0.83 |

$\beta = 1/n \sum (v_{\text{complex}}/v_{\text{aqueous}})$, $\delta = [(1-\beta)/\beta] \times 100$
Figure 1. Absorption spectra of a crystal of Nd(H$_2$C=CHCH$_2$COO)$_3$·2H$_2$O at low temperatures
Figure 1. Continued. Absorption spectra of a crystal of Nd(H$_2$C=CHCH$_2$COO)$_3$·2H$_2$O at low temperatures.
Figure 2. Absorption spectra of a crystal of Ho(H₂C=CHCH₂COO)₃·3H₂O
Figure 3. Fluorescence excitation spectra of a crystal of Eu(H₂C=CHCH₂COO)₃·2H₂O

Figure 4. Fluorescence spectra of Eu(H₂C=CHCH₂COO)₃·2H₂O
In the 1960’s Jörgensen proposed that the positions of the hypersensitive bands change due to the „nephelauxetic” effect\textsuperscript{12}. This effect may be used as a measure of the covalency of the Ln-L bond, in our case of the Ln-O bond. The nephelauxetic effect, in which the red shift observed for f-f energy differences with respect to the free ion, is related to a decrease in the values of the Slater integrals $F^k$ and the spin-orbit coupling parameter $\xi$. The nature of this effect has been already discussed in the literature\textsuperscript{12-14}. The „red shift” was observed by us not only for the hypersensitive but for the other transitions Ln$^{3+}$ ions, respectively (see Table 6). The size of the nephelauxetic effect can be characterised by the ratio $\beta$\textsuperscript{15}:

$$\beta = \frac{1}{n} \sum (\nu_{av(\text{complex})}/\nu_{av(\text{aquoion})})$$  \hspace{1cm} (1)

where $\nu_{av}$ is the average of the band position and $n$ is the number of transitions observed.

Sinha proposed a parameter $\delta$ which was used to measured the ‘degree of covalency’\textsuperscript{15}:

$$\delta = \{(1 - \beta)/\beta\} \times 100$$  \hspace{1cm} (2)

The results for the title compounds are presented in Table 6 for all compounds, 0.83 $> \delta >$ 0.05, which indicates weak covalent Ln-O bonds. The variations of the Sinha’s parameter $\delta$ for Ln(C$_2$H$_4$O$_2$)$_3$2H$_2$O and Ln(C$_6$H$_5$O$_2$)$_3$2H$_2$O point out that this dependence is not linear (it has a minimum for the Eu$^{3+}$ ion). The covalency of the Ln-O bond depends on the metal atomic number and it increases in a bigger rate than the ionic one as the metal atomic number increases. The purely phenomenological covalency parameter $\delta$ has shown a good correlation with the observed „red shifts” (see Table 6). The parameters, determined on the basis of the absorption spectra: the nephelauxetic ratio $\beta$ and Sinha’s parameter $\delta$ and their variations for Ln(C$_2$H$_4$O$_2$)$_3$2H$_2$O (I) and Ln(C$_6$H$_5$O$_2$)$_3$2H$_2$O (II) point out that the degree of Ln$^{3+}$–L bond covalency is rather bigger for the II than I compounds, it means for the compound with the shorter “C-chain” in the ligand.

One of the parameters, which can determine the degree of Ln$^{3+}$–L bond covalency, is a strength of the vibronic coupling for the 4f–4f transitions of Ln$^{3+}$ ions. Therefore, the quantitative estimation of the vibronic coupling is of great importance. The vibronic coupling strength observed in the investigated compounds is rather bigger for heavier ions such as Ho$^{3+}$ than for the Nd$^{3+}$ ion (see Table 6). The vibronic coupling strength is less expected for the ionic compounds than for compounds with covalent bonds. The same relation was observed by us for the lanthanide chloride single crystals\textsuperscript{16}.

Generally, the spectroscopic results presented in this paper have demonstrated that these methods can be a good instrument to investigate the nature of Ln-L bond. This is very important when considering the potential applications of the lanthanide carboxylates in catalysis.

Conclusions

1. The high values of the absorption spectral intensities at 293 K for Ln(C$_2$H$_4$O$_2$)$_3$2H$_2$O (where Ln = Pr, Nd, Eu; C$_4$H$_8$O$_2$ = 4-pentenoic anion (I)) and Ln(C$_6$H$_5$O$_2$)$_3$2H$_2$O (where Ln = Pr, Nd, Eu, Ho, Er; C$_6$H$_5$O$_2$ = 3-butenolic anion (II)) show only a low symmetry of the metal centre (i.e. high values of: a) the oscillator strength of the hypersensitive transitions, b) the $t_2$ parameters).
2. The intensity decrease of some transitions with decreasing temperature was observed for the Nd$^{3+}$ and Ho$^{3+}$ ions for the crystals of the investigated compounds. It is attributed to the electron-phonon coupling and/or depopulation of the Stark components of the ground state multiplet. This fact demonstrates the contribution of a vibronic mechanism to the intensities of electronic transitions.
3. The parameters determined on the basis of the absorption spectra: the nephelauxetic ratio $\beta$ and Sinha’s parameter $\delta$ and their variations forLn(C$_2$H$_4$O$_2$)$_3$2H$_2$O and Ln(C$_6$H$_5$O$_2$)$_3$2H$_2$O point out that this dependence is not linear (minimum for the Eu$^{3+}$ ion). The covalency of the Ln-O bond depends on the metal atomic number and it increases in a bigger rate than the ionic one as the metal atomic number increases. One of the parameters, which can determine the degree of Ln$^{3+}$–L bond covalency, is a strength of vibronic coupling for the 4f–4f transitions of Ln$^{3+}$ ions. Therefore, the quantitative estimation of the vibronic coupling is of great importance.


\textsuperscript{16} G. Oczko, L. Macalik, Polyhedron, 2009, in press.
4. In the low temperature spectra vibronic components are very well observed as sidebands or additional very weak lines. Assignments of particular vibronic components, made using the IR data, indicate that they correspond mainly to the stretching v(Ln-O) and lattice modes. It seems that these low wavenumber modes play an important role in the electron-phonon coupling. The vibronic coupling strength observed in the investigated compounds is rather bigger for heavier ion such as Ho$^{3+}$ than for the Nd$^{3+}$ ion.

5. The parameters determined on the basis of the absorption spectra: the nephelauxetic ratio $\beta$ and Sinha’s parameter $\delta$ and their variations for Ln(C$_5$H$_7$O$_2$)$_3$·2H$_2$O (I) and Ln(C$_5$H$_7$O$_2$)$_3$·2H$_2$O (II) point out that the degree of Ln$^{3+}$–L bond covalency is rather bigger for the II than I compounds.

6. Generally, the spectroscopic results presented in this paper have demonstrated that these methods can be a good instrument to investigate the nature of Ln-L bond, which is very important when considering the potential applications of the lanthanide carboxylates in catalysis.

**Experimental**

The lanthanide compounds of the formula Ln(C$_5$H$_7$O$_2$)$_3$ (I) (Ln = Pr, Nd, Eu) and Ln(C$_5$H$_7$O$_2$)$_3$ (II) (Ln = Pr, Nd, Eu, Ho, Er) were synthesised by slow reaction between their oxides and 4-pentenoic (I) or 3-butenolic (II) acid at controlled pH ($\approx$5.2) and temperature ($\approx$55°C). The lanthanide oxides and both acids were of commercial grade and were used without further purification. Single crystals of Nd(H$_2$C=CH-CH$_2$COO)$_3$·2H$_2$O and Ho(H$_2$C=CH-CH$_2$COO)$_3$·3H$_2$O of good optical quality were obtained by evaporation of the solutions. The contents of lanthanide ions were determined by complexometric EDTA titration with xylonol orange as indicator.

Crystal densities were measured by the flotation method using dichloromethane and ethylene dibromide and were $\rho_{20} = 1.702$ g cm$^{-3}$ and $\rho_{30} = 1.786$ g cm$^{-3}$ for the neodymium and holmium carboxylate, respectively.

High resolution absorption spectra of Ln(C$_5$H$_7$O$_2$)$_3$ (I) (Ln = Pr, Nd, Eu) and Ln(C$_5$H$_7$O$_2$)$_3$ (II) (Ln = Pr, Nd, Eu, Ho, Er) solutions were recorded within the spectral range 300 - 2200 nm at 293 K and for single crystals of Nd(H$_2$C=CH-CH$_2$COO)$_3$·2H$_2$O and Ho(H$_2$C=CH-CH$_2$COO)$_3$·3H$_2$O at 4.2 K using a Cary-Varian 500 UV-Vis-near-IR spectrophotometer equipped with an Oxford CF 1204 continuous flow helium cryostat. The areas of the absorption bands were determined numerically by a graphical integration method and expressed in terms of the experimental oscillator strengths values were used for the calculation of Judd-Ofelt parameters $\tau_\lambda$ [cm]$^2$ according to the equation in the form given by Carnall$^{4,5}$:

$$P = 4.33 \times 10^{-9} \int_\sigma^\sigma_1 \varepsilon(\sigma)d\sigma,$$

where $\varepsilon(\sigma)$ is the molar extinction coefficient of the band at the wave number $\sigma$ [cm$^{-1}$].

The experimental oscillator strengths values were used for the calculation of Judd-Ofelt parameters $\tau_\lambda$ [cm]$^2$ according to the equation in the form given by Carnall$^{4,5}$:

$$P = \sum_{\lambda=2,4,6} \tau_\lambda \sigma \left( f^N \Psi_f \left| U^{(l)} \right| f^N \Psi_{f'} \right)^2 \left(2J + 1\right),$$

where $(f^N \Psi_f \left| U^{(l)} \right| f^N \Psi_{f'})$ are the reduced matrix elements of the unit tensor operator $U^{(l)}$ calculated by Carnall et al.$^{4,5}$ in the intermediate coupling scheme, $\Psi_f$, $\Psi_{f'}$ are the initial and final states of the electronic transition and J is the total quantum number.

The emission and emission excitation spectra of the europium title solutions were recorded at 293 and 77 K using the SLM AminoCo SPF 500 spectrophotofluorometer. The IR spectra, in nujol and KBr pellets, were recorded in the range of 50 - 4000 cm$^{-1}$ with a Brucker IFS66 spectrophotometer.

Received: September 15, 2009.

Cytotoxicity of Gd$_2$O$_3$:Ln$^{3+}$ Nanostructures and their Potential as Biomarkers

Eva Hemmer$^*$, 1, Tomoyoshi Yamano$^2$, Hidehiro Kishimoto$^2$, 3 and Kohei Soga$^1$

1 Department of Materials Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan; 2 Research Institute for Biological Sciences, Division of Immunobiology, Tokyo University of Science, 2669 Yamazaki, Noda, Chiba 278-0022, Japan; 3 Center for Technologies against Cancer, Tokyo University of Science, 2669 Yamazaki, Noda, Chiba 278-0022, Japan
E-mail: eva.hemmer@sogalabo.jp

Abstract. In this study erbium and ytterbium doped gadolinium oxide nanostructures were synthesized. To investigate the influence of morphology on the optical and biological properties of the obtained particles, different types of nanoparticles were prepared. First, Gd(OH)$_3$:Er$^{3+}$,Yb$^{3+}$ nanorods of aspect ratios of 5 and 12 were synthesized by hydrothermal method, which could be transformed into the oxide phase by post-thermal treatment. Enzymatic and alkaline precipitation methods were used to prepare nanoparticles of approx. 40 nm in diameter and larger particles with less homogeneous size distribution in the range from 100 nm to 1 µm, respectively. Spherical particles of 300 nm in diameter and with a homogeneous size distribution were obtained by homogeneous precipitation. Investigation of their optical properties, in particular upconversion emission and near-infrared emission, revealed the potential use of the obtained nanostructures for applications as biomarkers. In this context, morphology and size effects on the cytotoxicity of Ln$^{3+}$-doped gadolinium oxide were investigated using B-cell hybridomas and macrophages. Concentrations of particles up to 500 µg/mL at an incubation period of 48 hrs were analyzed.

Keywords: Gadolinium Oxide; Cytotoxicity; Upconversion Luminescence; Biomarkers

Introduction

Fluorescent markers like commonly used organic dyes or recently investigated quantum dots have been applied for bioimaging, but suffered from colour fading and their toxicity. Further problems are auto-fluorescence and photo toxicity as well as scattering when ultraviolet light is used as excitation source. The outstanding optical and magnetic properties of lanthanides make inorganic materials doped with lanthanide ions be promising candidates to overcome these problems. Recently, upconverting phosphors that absorb infrared radiation and emit in the visible spectrum like Er$^{3+}$-doped Y$_2$O$_3$ are attracting attention and were successfully applied in fluorescence biolabeling$^{1,2}$.

Ongoing with the wide range of potential applications of nanomaterials in biomedicine, which includes drug delivery and controlled release, active surfaces and bio-markers in cell-tracking or diagnostics studies$^{3,4,5}$, there is an increasing necessity of understanding the interactions between engineered inorganic nanomaterials and biological tissue. In this context, a range of risk management options has been developed$^6$ and numerous studies addressed the toxicology of nanostructures in recent years$^{7,8,9}$. These studies clearly showed that nanostructures can be taken up in vivo via respiratory tract, gastrointestinal tract and skin and further distribution from initial

---

exposure location to other bodily parts must be considered. While most of the published cytotoxicity studies on metal oxides deal with transition metal oxides like TiO$_2$, ZrO$_2$, Al$_2$O$_3$ or Fe$_2$O$_3$, there are only few reports on Ln$_2$O$_3$ or Ln(OH)$_3$.

Therefore, our interest is focused on the synthesis of lanthanide containing inorganic materials suitable for applications as biomarkers, whereas the investigation of the cytotoxic behaviour in dependence of particle morphology is an aspect of particular interest. In this study, erbium and ytterbium doped gadolinium oxide nanostructures, Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ (1 mol% doping), were synthesized. In order to investigate the influence of morphology on the optical and biological properties of the obtained particles, different types of nanostructures, nanorods and nanoparticles of various size, were synthesized by hydrothermal and precipitation methods. Their cytotoxic effect on B-cell hybridomas as well as macrophages was analyzed by various in vitro assays.

Results and Discussion

Materials Synthesis and Characterization

Erbium and ytterbium doped gadolinium oxide nanostructures were prepared by hydrothermal as well as precipitation methods using lanthanide nitrates, Ln(NO$_3$)$_3$$\times$H$_2$O, as starting material, whereas variation of process parameters allows the control of size and morphology as shown in Fig. 1.

Figure 1. SEM images of erbium and ytterbium doped Gd(OH)$_3$ (a) and Gd$_2$O$_3$ nanostructures obtained by hydrothermal synthesis (b, c), alkaline (d), homogeneous (e) and enzymatic (f) precipitation methods.

Scanning electron micrographs of the as-prepared powder obtained by hydrothermal synthesis using an aqueous potassium hydroxide solution as precipitant reveals elongated structures with homogeneous length of several hundred nanometres and a diameter of approximately 40 nm (Fig. 1a). Due to the ratio of length and diameter (aspect ratio: $\sim$ 12) the obtained nanostructures can be classified as nanorods. The X-ray diffraction pattern of the respective powders matches with reference data for crystalline gadolinium hydroxide, Gd(OH)$_3$ (Fig. 2). Due to crystallization of gadolinium hydroxide in the hexagonal lattice ($a = 6.3290$ Å, $c = 3.6310$ Å) anisotropic growth is favoured. Therefore, no templates are required to prepare elongated structures. Post-thermal treatment

---

of the as-prepared Gd(OH)$_3$:Er$^{3+}$,Yb$^{3+}$ nanorods at 900 °C for 30 min results in crystalline gadolinium oxide as shown by XRD measurements (Fig. 2), while the rod-like morphology has been retained (Fig. 1b).

Figure 2. X-ray diffraction patterns of as-prepared and post-annealed (T = 900 °C) powders obtained by hydrothermal synthesis. Reference files: Gd(OH)$_3$ [PDF 83-2037], Gd$_2$O$_3$ [PDF 12-0797].

Variation of the aspect ratio is possible by use of different precipitation agents. When an aqueous ammonia solution was chosen instead of KOH$_{aq}$, aspect ratio of the resulting nanorods was reduced from 12 to 5 (Fig. 1c).

While hydrothermal treatment resulted in nanorods, spherical particles were obtained by precipitation methods. In general, precipitation method results in amorphous precursors, which must be post-thermally treated in order to transform them into crystalline oxides$^{13}$. Hereby, high temperatures (900 °C) are necessary to eliminate residual hydroxyl and carbonate groups. Alkaline precipitation using sodium carbonate, Na$_2$CO$_3$, as precipitation agent, resulted in particles of inhomogeneous morphology and size (d ~ 100 nm – 1 µm, Fig. 1d). In contrast, homogeneous precipitation, during which the thermal decomposition of urea provides NH$_4^+$ acting as precipitation agent$^{14}$, led to homogeneous nanoparticles of approximately 300 nm in diameter (Fig. 1e). Smaller particles of less than 100 nm in diameter can be obtained by enzymatic precipitation. In this method the enzyme urease is used in order to decompose urea at room temperature providing NH$_4^+$, which reacts as precipitant. However, it must be mentioned that no surfactant was used in this study. Due to this, the small size particles show a high tendency to form agglomerations.

Optical properties of the powders obtained by hydrothermal synthesis (precipitant: KOH$_{aq}$), alkaline and enzymatic precipitation were investigated with regard to upconversion and near infrared emission. Upconversion emission spectra of the erbium and ytterbium doped gadolinium oxide powders were recorded under an excitation of 980 nm and are given in Fig. 3a.

Figure 3. (a) Upconversion and (b) near infrared emission (T = room temperature) of Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ nanostructures obtained by enzymatic (A) and alkaline (B) precipitation method as well as hydrothermal synthesis (precipitant: KOH$_{aq}$) (C).

14 E. Matijevic, W. P. Hsu, J. Colloid Interface Sci. 1987, 118, 506.

© 2010 NWT-Verlag, Bornheim, Germany
All spectra show the characteristic peaks due to Er\(^{3+}\) f-f transitions. The observed bands are referred to \(^{4}I_{11/2} \rightarrow ^{4}I_{15/2}\) (523 nm, 538 nm), \(^{4}S_{3/2} \rightarrow ^{4}I_{15/2}\) (550 nm, 561 nm) and \(^{4}F_{9/2} \rightarrow ^{4}I_{15/2}\) (659 nm, 673 nm, 680 nm) transitions. Highest intensities were recorded in case of the sample obtained by alkaline precipitation. For clearer display, a filter (ND50) was used in order to obtain intensities in the same range as for the samples obtained by hydrothermal synthesis and enzymatic precipitation. Differences in the intensity and shape of the emission spectra, in particular differences in the ratio between the intensity of the \(^{4}S_{3/2} \rightarrow ^{4}I_{15/2}\) transition and the intensity of the \(^{4}F_{9/2} \rightarrow ^{4}I_{15/2}\) transition, cannot be clearly explained, but may be due to different powder densities or various carbonate or hydroxyl impurities in dependence of the preparation method.

Fig. 3b shows the emission of light in the near infrared region of the spectrum when powders are excited at 980 nm. A maximum peak is obtained at 1540 nm, which can be attributed to the \(^{4}I_{11/2} \rightarrow ^{4}I_{15/2}\) transition of Er\(^{3+}\). The peak of lower intensity at a wavelength of 1078 nm is due to the Yb\(^{3+}\) emission.

### Cytotoxicity Tests

The observation of upconversion and near infrared emission makes the investigated Gd\(_2\)O\(_3\):Er\(^{3+}\),Yb\(^{3+}\) powders to promising candidates for bioimaging. However, with regard to applications in medicine, it is essential to investigate the cytotoxic behaviour of the samples. Therefore, nanostructure concentrations from 1 to 500 µg/mL were incubated for 48 hrs with two different cell types: B-cell hybridomas and macrophages. The later were chosen because they are well known to have phagocytic ability that uptakes foreign material.\(^{15}\)

The cytotoxic effects of the nanomaterials were evaluated by cell counting using a hemocytometer, utilizing \([\text{H}]-\text{Thymidine proliferation assay as well as CFSE (carboxylfluorescein diacetate succinimidyl ester) assay. For comparison, each assay was additionally effected after incubation of both cell types in medium alone representing ideal incubation conditions and whose results were set as 100 % viability (negative control) as well as after incubation with the anti-cancer drug carboplatin provoking cell death (positive control).}

Viability of B-cell hybridomas as a function of morphology and concentration was determined by cell counting after incubation, followed by staining of the dead cells with the dye trypan blue. As obvious from Fig. 4, no significant decrease of viability was observed and viabilities of almost 100 % were obtained for all samples, independent from morphology and concentration.

![Figure 4. Viability of B-cell hybridomas after 48 hrs incubation with Gd\(_2\)O\(_3\):Er\(^{3+}\),Yb\(^{3+}\) nanostructures (determined by dye exclusion test).](image-url)

Proliferation rate of B-cell hybridomas after 48 hrs incubation was determined using the CFSE assay. The cytoplasmic dye CFSE is used to quantify cell division. When a CFSE labelled cell divides, CFSE is divided equally between the two daughter cells. Provided that the initial cell labelling is relatively homogeneous, this leads to a characteristic flow cytometric profile where a number of peaks of progressively halving CFSE fluorescence intensity are observed. By analysing these data, the average proliferation rate and the average death rate of B-cell hybridomas can be estimated\(^{16, 17}\). From fluorescence intensity the rate of divided cells after 48 hrs of incubation with different Gd\(_2\)O\(_3\):Er\(^{3+}\),Yb\(^{3+}\) morphologies and concentrations was deduced and results are


presented in Fig. 5a. Lowest division rate (96.2%) was observed in case of nanorods with an aspect ratio of approximately 12 (hydrothermal synthesis, precipitant: KOH$_{aq}$) at a concentration of 100 µg/mL. These results confirm the high viability determined by cell counting. Hence, according to data obtained by CFSE assay, Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ induced no significant decrease of the proliferation activity up to the highest tested concentrations (100 µg/mL) and independent from morphology.

Further, proliferation rates of B-cell hybridomas incubated with Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ nanorods of an aspect ratio of 12 (hydrothermal synthesis), and nanoparticles of several 100 nm in diameter (alkaline precipitation), respectively approximately 40 nm in diameter (enzymatic precipitation) were measured by means of the $[^3$H]-Thymidine incorporation assay. $[^3$H]-Thymidine is a labeled DNA precursor. Before a cell divides, its DNA is replicated and precursors are incorporated, thus if the cells are proliferating and $[^3$H]-Thymidine is added to the culture, it will be incorporated into the cells’ DNA. Herein, the observed radioactivity directly correlates with DNA synthesis, thus, a high radioactivity corresponds to high proliferation rate.

**Figure 5.** (a) Proliferation rate of B-cell hybridomas incubated with Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ nanostructures for 48 hrs (CFSE assay). (b) Radioactive rate of B-cell hybridomas after 48 hrs incubation with Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ and $[^3$H]-Thymidine.

**Figure 6.** Living / dead staining of B-cell hybidomas after 48 hrs incubation with Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ nanostructures obtained by (a) hydrothermal synthesis, (b) alkaline and (c) enzymatic precipitation as well as after 48 hrs incubation in (d) medium only (negative control) and (e) with carboplatin (positive control).
As given in Fig. 5b, radioactivity, and hereby proliferation rate, showed lowest values in case of nanoparticles with a diameter of approximately 40 nm obtained by enzymatic precipitation. At lowest concentration (1 µg/mL), radioactivity decreases from 9649 counts in case of nanorods (l/d ~ 12) to 8556 counts in case of the nanoparticles of 40 nm diameter. Further decrease in case of the smallest nanoparticles is observed at higher Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ concentrations: 6886 counts for 10 µg/mL, respectively 6825 counts for 100 µg/mL. However, it must be taken in account that all radioactivity values obtained after incubation with Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ nanostructures are higher than in case of the negative control (5920 counts). This observation may indicate a positive effect of the nanostructures on cell proliferation, but further investigations are necessary for confirmation.

Additionally to the cytotoxicity test a living / dead staining was performed. Therefore, propidium iodide (PI) was added to the culture of CFSE labelled cells. PI is a fluorescent molecule and binds to double-stranded DNA, but it can only cross the plasma membrane of non-viable cells. All fluorescence images were taken after 48 hrs of exposure. Hereby, living cells are stained by the green fluorescing compound CFSE; dead cells appear red due to PI. The high percentage of green fluorescing cells (Fig. 6) confirms the results obtained by cell counting and cytotoxicity assays.

According to the above described results of cell counting, CFSE and [$^3$H]-Thymidine assay as well as living / dead staining, no inhibitory effect on cell proliferation and viability by the investigated Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ nanostructures was observed. It is interesting to mention that the expected influence of nanostructure morphology on cytotoxic effect was not observed. This may be due to the fact that in particular the small nanoparticles show a high tendency to agglomerate as observed in SEM. Consequently, in case of all three investigated samples (nanorods with an aspect ratio of 12, nanoparticles of several 100 nm in diameter and nanoparticles of about 40 nm) larger clusters of nanostructures were in contact with the cells resulting in similar effective diameters of powder agglomerations and therefore similar bio-nano interactions.

In order to avoid agglomerations, in a second experiment, nanostructures were sterilized in ethanol instead of autoclavage, because the later one may facilitate the formation of agglomerates, followed by sonication of the nanostructure cell culture medium mixture to break down larger agglomerates. Further, less agglomerated particles of homogeneous size (300 nm) could be obtained by homogeneous precipitation. These particles, as well as nanorods of two different aspect ratios, 12 respectively 5, were incubated with B-cell hybridomas and macrophages in order to investigate the influence of the chosen cell line on cytotoxicity of Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ nanostructures. Due to the fact that previous experiments with concentrations of particles up to 100 µg/mL did not show any cytotoxic effect, 500 µg/mL was chosen as highest concentration in the following investigation.

After incubation for 48 hrs with B-cell hybridomas viability was determined by cell counting. Again, viabilities of almost 100 % independent from morphology and concentration were observed. However, in contrast to B-cell hybridomas a significant decrease in viability was observed when the nanostructures were incubated with macrophages (Fig. 7).

![Figure 7. Viability of macrophages after 48 hrs incubation with Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ nanostructures (determined by dye exclusion test).](image-url)
Highest viability was determined after incubation of nanorods with an aspect ratio of 12 at a concentration of 125 µg/mL, namely 67 %, which represents a significant decrease when compared to the negative control. Incubation with nanorods with an aspect ratio of 5 at a concentration of 250 µg/mL resulted in lowest viability (22 %). The authors suggest the poor chemical stability of Ln₂O₃ under acidic conditions as a potential reason for the cytotoxic effect. Macrophages tend to phagocyte foreign materials, so the nanoparticles. Due to the acidic condition inside the macrophages (pH ~ 3.5) gadolinium oxide may partially be dissolved resulting in the presence of Gd³⁺ ions, which may reduce viability of the macrophages. Recently, further investigations are undertaken to verify this assumption.

**Effect of Cell Culture Medium on Surface Properties**

The effect of incubation in cell culture medium on surface chemistry of the Gd₂O₃:Er³⁺,Yb³⁺ nanostructures was investigated by FT-IR spectroscopy. The obtained spectra of as-prepared and incubated nanoparticles obtained by homogeneous precipitation are shown in Fig. 8. Similar spectra are observed for nanorods (l/d ~ 5 and 12). In case of the as-prepared sample, the spectrum shows a strong band in the range of 500 cm⁻¹ which can be assigned to the M-O bonds in the oxide phase. The lower band at the range of 1500 cm⁻¹ is due to C=O bonds and may originate from carbonate contamination. The spectrum obtained for powders incubated in cell culture medium for 24 hrs shows three major differences when compared to the as-prepared sample. The broad band at 3500 cm⁻¹ corresponds to the O-H stretching vibration due to hydroxide groups. Further, an increase in intensity of the peaks at 1512 and 1390 cm⁻¹ as well as an additional peak at 1642 cm⁻¹ are observed, which can be assigned to C=O and N-H bonds and may be due to adsorption of amino acids from the cell culture media on the particle surface. A strong peak at 1070 cm⁻¹ indicates the presence of P=O groups resulting from the phosphate containing cell culture medium (RPMI-1640 medium: 0.8 g/L anhydrous sodium phosphate dibasic). Similar spectra have been reported by Tkaczyk et al. who investigated formation of chromium(III) complexes in simulated physiological fluids and have been observed in our own investigation of the cytotoxicity of gadolinium hydroxide nanostructures.

**Figure 8.** FT-IR spectra of annealed powders obtained by homogeneous precipitation (A) and after 24 hrs incubation in cell culture medium (B).

Upconversion emission spectra of as-prepared and in cell culture medium incubated nanoparticles obtained by homogeneous precipitation are presented in Fig. 9a. Both spectra show the characteristic peaks for the f-f transitions of Er³⁺ ions as already described above (Fig. 3a). Peak intensity for the incubated particles decreased, which can be assigned to quenching effects due to hydroxyl groups attached at the surface as revealed by FT-IR spectroscopy.

For investigation of the optical properties of the nanoparticles under physiological conditions, Gd₂O₃:Er³⁺,Yb³⁺ nanoparticles were incubated with B-cell hybridomas for 48 hrs and the cell culture system was analyzed in

---

fluorescence microscope. The fluorescence image obtained for the respective sample under excitation with infrared light of 980 nm wavelength shows the characteristic upconversion emission of Er$^{3+}$ ions in the green range of the visible spectrum, even in aqueous medium (Fig. 9b).

Figure 9. (a) Upconversion emission spectra of annealed powders obtained by homogeneous precipitation (A) and after incubation in cell culture medium (B). (b) Fluorescence microscope image of Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ particles incubated with B-cell hybridomas (48 hrs) under physiological conditions ($\lambda_{ex} = 980$ nm, $P = 700$ mA).

### Experimental Section

#### Material Synthesis

Starting materials like lanthanide nitrates (Ln = Gd, Er, Yb), sodium carbonate, urea, urease enzyme, potassium hydroxide and ammonia were purchased from usual commercial sources and were used without further purification.

For alkaline precipitation, 4 mmol Gd(NO$_3$)$_3$·6H$_2$O were dissolved in 100 ml distilled water. To obtain Gd$_2$O$_3$ particles doped with 1 mol% of Er$^{3+}$ and Yb$^{3+}$ 0.041 mmol Er(NO$_3$)$_3$·5H$_2$O and 0.041 mmol Yb(NO$_3$)$_3$·xH$_2$O were added to the gadolinium nitrate solution. An aqueous Na$_2$CO$_3$ solution (c = 0.5 mol/l, V = 100 ml) was added to the lanthanide nitrate solution and stirred at room temperature for 2 hrs. For homogeneous precipitation, 3 mmol Gd(NO$_3$)$_3$·6H$_2$O and 1 mol% Er(NO$_3$)$_3$·5H$_2$O, respectively Yb(NO$_3$)$_3$·xH$_2$O were dissolved in 300 ml H$_2$O and 150 mmol urea were added. The mixture was stirred at 85 °C for 2 hrs. 3 mmol Gd(NO$_3$)$_3$·6H$_2$O and 1 mol% Er(NO$_3$)$_3$·5H$_2$O, respectively Yb(NO$_3$)$_3$·xH$_2$O were dissolved in 200 ml H$_2$O in case of enzymatic precipitation and 0.3 mol urea were added. This solution was added to an aqueous urease solution (22.5 mg urease in 100 ml H$_2$O) to initiate precipitation. The mixture was stirred at room temperature for 2 hrs. In hydrothermal synthesis, the concentration of gadolinium nitrate was set to 0.05 mol/l at a total volume of 30 ml. Therefore, in a first approach 1.5 mmol Gd(NO$_3$)$_3$·6H$_2$O and an appropriate amount of Er(NO$_3$)$_3$·5H$_2$O and Yb(NO$_3$)$_3$·xH$_2$O were dissolved in 25.5 ml H$_2$O. The obtained solution was transferred in Teflon liners (V = 50 ml) and activated with 4.5 ml 1M aqueous KOH solution. In a second approach, 1.5 mmol Gd(NO$_3$)$_3$·6H$_2$O and an appropriate amount of Er(NO$_3$)$_3$·5H$_2$O and Yb(NO$_3$)$_3$·xH$_2$O were dissolved in 29.0 ml H$_2$O and the mixture was activated by addition of 1 ml of aqueous ammonia hydroxide (aqueous solution, 25 %). After enclosing the Teflon liners in steel autoclaves, autoclaves were placed in a furnace and heated to a temperature of 200 °C that was kept for 12 hrs.

The obtained powders were collected by centrifugation, washed two times with distilled water and dried at 80 °C for at least 12 hrs. Crystalline oxide powders were obtained by post-thermal treatment at 900 °C (30 min).

#### Material Characterization

The crystalline phase of the samples was determined by powder XRD with a ULTIMA III diffractometer (Rigaku) using CuK$\alpha$ radiation. Morphology of the obtained powders was investigated by scanning electron microscope (S-4200, Hitachi). For FT-IR spectroscopy, samples were mixed with KBr and spectra of the powders were recorded under vacuum conditions using a JASCO FT/IR-6500 spectrometer. Upconversion emission spectra were recorded at room temperature using a RF-5000 Spectrofluorometer by Shimadzu-Seisakusho under excitation by an IR diode laser at 980 nm. For near-infrared emission, samples were excited at room temperature with the aid of a Laser Diode by Hamamatsu Photonics K. K. (L9418-04, $\lambda_p = 977.7$ nm)
using a Thorlabs Laser Diode Controller 2A (LDC 220), Temperature Controller (TED 200) and Laser Diode Mount (6 mm / 9 mm). Near infrared emission was detected with a detection system Avantes (AvaSpec-NIR 256-1.7, NIRA, set for 969-1750 nm, Slit-50). Upconversion emission under physiological conditions was observed in a fluorescence microscope (IX71, Olympus) equipped with a near infrared source (TCLDM9, Thorlabs.). Therefore, a drop of a dispersion of powders incubated in cell culture medium was placed on a glass bottom dish and luminescence was measured under 980 nm excitation.

**Cytotoxicity Tests**

B-cell hybridomas (cell line: 53-6.7, purchased by ADCC) and macrophages (cell line: J774, purchased by ADCC) were used to evaluate cytotoxicity of the obtained particles using in vitro experimental protocols. B-cell hybridomas and macrophages were cultured in RPMI 1640 medium (Sigma-Aldrich) containing 10% FCS, 2ME, l-glutamin, penicillin/streptomycin, 0.1mM HEPES, non-essential amino acid and pyruvic acid. Incubation period was 48 hrs. Before incubation, the nanostructures were sterilized either by autoclavation or by use of 70% ethanol and the nanostructure culture medium mixture was sonicated for 5 min. Concentrations of the nanostructures in the cell culture media varied between 1 µg/mL and 500 µg/mL.

In a first assay, viability of B-cell hybridomas was analysed with trypan blue dye by counting cells in a hemocytometer. To determine viability of cells and division of cells, the CFSE assay was used. This assay is based on the transformation of the non-fluorescent and cell permeable compound CFSE (carboxylfluorescein diacetate, succinimidyl ester) into a fluorescent and cell impermeable compound when reacting with cellular esterase, which is synthesized during cell proliferation. In order to determine viability and cell dividing rate, B-cells hybridomas were stained with CFSE before cultivation, followed by staining with propidium iodide after incubation and performing of flow cytometric analysis. Cell proliferation rate was further determined by [³H]-Thymidine assay. This assay is based on the incorporation of the radionucleotide [³H]-Thymidine in newly synthesized DNA during cell division process, whereas the measured radioactivity of the incubated cells directly correlates with the proliferation rate. Viability of macrophages was solely determined by cell counting in a hemocytometer.

Living / dead staining was performed in order to confirm the results obtained by cytotoxicity assays. Therefore, cells were stained with CFSE and PI and analysed in a confocal microscope Leica TSC-SP2. As a positive control anti-cancer drug carboplatin (c = 100µg/mL, provided by Nihonkayaku) was used, which induced cell death. Incubation of cell culture medium without nanostructures demonstrated the negative control simulating cell behaviour under ideal conditions. All data obtained for incubated nanostructures were compared to the control.

For investigation of the surface modification by incubation in cell culture medium 50 mg of nanoparticles obtained by homogeneous precipitation were incubated with 25 ml of RPMI 1640 containing 10 % FCS for 24 hrs. After incubation, the samples were collected by centrifugation, washed twice with distilled water and dried in a freeze dryer (FDU-12AS by Ason Corporation) for 24 hrs.

**Conclusions**

Various erbium and ytterbium doped gadolinium oxide nanostructures (Gd₂O₃:Er³⁺,Yb³⁺) have been synthesized using lanthanide nitrates as starting materials. Variation of the synthesis process allowed the control of size and morphology of the obtained nanostructures. While rod-like nanostructures with an aspect ratio of 5, respectively 12 were obtained by hydrothermal synthesis, precipitation methods resulted in the formation of spherical particles. Hereby, particles obtained by alkaline precipitation showed an inhomogeneous morphology and size distribution (100 nm – 1 µm). Enzymatic precipitation provided particles smaller than 100 nm in diameter, which, tend to agglomerate. Finally, particles of a very homogeneous morphology and close size distribution (approximately 300 nm in diameter) were obtained by homogeneous precipitation method. The obtained samples were characterized with regard to their optical properties showing upconversion and near infrared emission under excitation with light of 980 nm wavelength independent from morphology.

Emission properties of the obtained powders make the samples promising candidates as biomarkers. With regard to potential applications in biomedicine cytotoxicity of the samples was investigated. Viability and proliferation rate of B-cell hybridomas as well as macrophages was analyzed after incubation with different concentrations of Gd₂O₃:Er³⁺,Yb³⁺ nanostructures (c = 1 – 500 µg/mL) by cell counting as well as use of [³H]-Thymidine proliferation assay and CFSE assay. In case of B-cell hybridomas no inhibitory effect on viability or proliferation rate was observed, independent from morphology and concentration. In contrast, we observed a cytotoxic effect in case of macrophages, which may be due to chemical instability of Gd₂O₃:Er³⁺,Yb³⁺ at pH 3.5 corresponding to the pH inside macrophages. Further, it was shown, that an in-situ surface modification of the nanostructures with phosphate groups takes place during incubation in cell culture medium. The presence of
phosphate groups may support the biocompatibility of Gd$_2$O$_3$:Er$^{3+}$,Yb$^{3+}$ when incubated with B-cell hybridomas. Incubated nanostructures showed upconversion emission, which even could be detected under physiological conditions in a fluorescence microscope.

These results show the potential of lanthanide containing inorganic materials for biomedical applications. However, it must be taken in account that the interaction between cells and nanostructures is still not completely understood, that there may be a need to modify currently used assays, and several independent tests are necessary to exclude any cytotoxic effect. In future, surface modification of our nanostructures will be investigated, which could not only avoid agglomerations, but may also facilitate the particle uptake by cells and herewith open new possibilities of lanthanide-based inorganic materials in biomedicine.

Acknowledgement
This work was partly supported by Matching Fund Subsidy from MEXT (Ministry of Education, Culture, Sports, Science and Technology), 2006-2010 and 2009-2013.

Received: November 10, 2009.
Abstract. Transparent single crystals of ytterbium doped LiGd$_6$O$_5$(BO$_3$)$_3$ have been grown by the flux method. The good optical quality enabled us to study spectroscopic properties. Absorption and emission spectra were recorded at room temperature. The emission spectrum exhibits several zero-phonon lines and a broad emission spectral range (from 975 to 1080 nm) due to the distribution of ytterbium ions in several types of coordination polyhedra. This characteristic is suitable for tunable laser application or ultra short pulses laser generation.

Keywords: Lanthanides; Solid State; Crystal Growth; Spectroscopy

Introduction

Borates are generally chemically stable over broad temperature ranges. Due to the versatility of borate groups connection, many compositions can be synthesized in both single crystalline or powder forms. The crystal structure of LiGd$_6$O$_5$(BO$_3$)$_3$ (LGOB) has been published in 1999. The unit cell is monoclinic (space group P2$_1$/c, Z=4) with a = 8.489(4) Å, b = 15.706(3) Å, c = 12.117(6) Å, β = 132.27(2)° (ρ = 6.706 g/cm$^3$). In this lattice, the rare earth elements (RE) are located in two eightfold GdO$_8$ polyhedra and four sevenfold GdO$_7$ polyhedra. They are connected by common edges and corners, giving rise to a three dimensional array. The oxyborate nomenclature comes from the fact that some oxygen atoms are located in ORE$_4$ tetrahedra. Strong chemical bonds between boron and oxygen atoms induce many distortions of the gadolinium coordination polyhedra. By doping this crystal host with optically active ions in several substitution locations, complicated fluorescence spectra are obtained. The range of applications is huge. One can list lighting (fluorescent lamp, diode), displays, high energy particles detection (scintillators) and all solid-state laser sources. In this latter topic, different doping ions can be introduced in the host lattice: trivalent neodymium, thulium or ytterbium ions are the most commonly used for their infrared spectroscopic properties. Ytterbium ions represent a good solution for diode pumped high power continuous wave (CW) lasers as


well as femtosecond, broadly tunable and compact near infrared (NIR) laser sources. The coordination and the Re-O distances determine the strength and the symmetry of the crystal field around Re elements and, consequently the splitting of the two \( ^{2}F_{5/2} \) and \( ^{2}F_{7/2} \) energy levels of trivalent ytterbium which is related to the broadening of the emission bands.

We recently reported the trivalent ytterbium doped \( \text{LiY}_6\text{O}_3(\text{BO}_3)_3 \) powder spectroscopic properties in the ultraviolet and the near infrared spectral ranges. The characteristics of the spectroscopic properties encouraged us to go further in this investigation by growing the material in single crystalline form.

**Experimental Section**

**Crystal growth**

LGOB decomposes with a peritectic transformation at 1080°C. An appropriate flux has to be identified to grow LGOB in single crystalline form. We propose in this investigation to use the pseudo-ternary diagram Li\(_2\)O-B\(_2\)O\(_3\)-Gd\(_2\)O\(_3\). This diagram exhibits an interesting pseudo-binary system between two compounds: LGOB oxyborate and Li\(_6\)Gd(BO\(_3\))\(_3\) (LGB) borate (Figure 1a). The melting point of LGB is equal to 860°C which makes it a good solvent to be used for the LGOB high temperature solution growth.

![Figure 1](image1.png)

**Figure 1.** a) Pseudo-binary system used to grow LGOB single crystals and b) obtained single crystals.

Two runs of single crystal growth were undertaken: low molar fractions of 8% (solution A) and 10% (solution B) of LGOB as solute in order to both avoid the decomposition of LGOB above 1080°C during the growth process and minimize the flux volatilization. A stable melt was obtained between 860°C and 1080°C. The global crystal growth process is reported in ref. 9. 10 mm long and 5 mm thick single crystals were grown with both solutions (Figure 1b). They exhibit large transparent regions. White cloudy inclusions mainly located in the vicinity of the initial seed are also visible. LGOB single crystals present natural facets.

**Chemical and physical characterizations**

Chemical analysis was performed by ICP on Varian 720-ES equipment. A concentration of 4.5% (molar substitution) of ytterbium was obtained which corresponds to \(8.88 \times 10^{20}\) ions/cm\(^3\).

Miller indices of five facets were determined by X-Ray diffraction patterns on a single crystal: \((\overline{1}11)\), \((\overline{1}00)\), \((1\overline{1}1)\), \((0\overline{2}1)\) and \((0\overline{2}1)\). A single crystal was selected and was optically polished on a Logitech Ltd system. The X-ray data indicate that the orientation of the selected plate is \((\overline{1}H\overline{2})\). The total thickness after surface treatment is 1.2 mm.

A refractive index of 1.93 ± 0.01 was determined at 532 nm using an extended Brewster angle method over the wide ± [10°; 80°] range of incident angle (reflected R\(_{\parallel}\) signal). Details about the procedure can be found elsewhere.

A value of 930 HK 0.1, corresponding to class 7 in Mohs’ scale Hardness measurement was obtained on a Leica VMHT.

Luminescence spectroscopy
Luminescence spectroscopy was performed on a Fluorolog 3 Horiba Jobin-Yvon spectrometer equipped with a nitrogen cooled InGaAs infrared detector. Parallel to the single crystal characterization, concentration studies have been performed on a powder sample. The emission spectra recorded for an excitation at 932 nm and concentration quenching curve are represented on Figure 2.

![Figure 2](image)

**Figure 2.** a) Emission spectra at room temperature as a function of the Yb$^{3+}$ concentration and b) the corresponding integrated intensity.

The maximum of the emission intensity is obtained for a 5% ytterbium content. The oxyborate LiGd$_6$O$_5$(BO$_3$)$_3$:Yb$^{3+}$ shows several intense lines around 974 nm which can be attributed to the zero line transition of ytterbium (transition from the level 5 down to the level 0, see inset in Fig. 2a). This clearly indicates that the dopant is located in several coordination polyhedra. In LGOB, the multiplicity of these 5→1 lines reflects the multiplicity of the ytterbium environment. The variation of the local crystal field leads to different splittings of the ytterbium ions Stark components. At higher wavelengths, the intensity decreases down to 1100 nm. However other maxima can be pointed at 1025 nm, 1035 nm, 1055 nm and 1088 nm. The attribution of the emission lines at the lowest energy part of the spectra is not easy because of the broadening of the lines (electron-phonon coupling) and the superposition with emission lines from different levels.

Absorption and emission spectra were also recorded on single crystals at room temperature. Figure 3 displays the absorption and emission cross-sections of Yb$^{3+}$ doped LGOB. Ytterbium emission was collected for an excitation at 932 nm in the 4f levels.

![Figure 3](image)

**Figure 3.** Absorption and emission cross section ($\lambda_{exc}$= 932 nm) of Yb$^{3+}$ doped LGOB.

The maximum of the absorption cross section, which corresponds to the 1→5 lines, is equal to 1.9×10$^{-20}$ cm$^2$. The total broadening of the absorption spectrum is about 900 cm$^{-1}$. Emission cross section was
calculated with the Füchtbauer–Ladenburg (equation 1) using the infrared emission spectrum, the decay time and the refractive index value ($\tau = 1.19$ ms, $n = 1.93$). The total broadening of the emission lines is about 1070 cm$^{-1}$.

**Equation 1.**

$$\sigma_{\varepsilon}(\lambda) = \frac{\lambda^4}{8\pi n^2 \tau} \int_{0}^{\infty} \frac{H(\lambda)}{H(\lambda)} d\lambda$$

Where $H(\lambda)$ is the emission spectrum, $n$, the refractive index and $\tau$, the decay time of the emission.

Table 1 lists spectral characteristics of other well-known laser crystals. For a better understanding, the emission bandwidth was measured by considering the FWHM gain cross-section for a partially excited-state population ($\beta = 0.5$ in equation 2). LGOB FWHM is equal to about 50 nm. The emission bandwidth of Yb-GdCOB$^{11}$ and Yb-BOYS$^{12}$ crystals is equal to 44 nm and 60 nm, respectively. Their laser performances lead to generation of ultra short pulses equal to 89 fs and 69 fs respectively.

**Table 1.** Single crystal spectroscopic characteristics

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{\sigma}^B$ (10$^{-20}$ cm$^2$)</th>
<th>FWHM (nm)</th>
<th>Experimental pulse time (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LGOB</td>
<td>1.9</td>
<td>0.03</td>
<td>0.34</td>
</tr>
<tr>
<td>GdCOB$^{11}$</td>
<td>1.1</td>
<td>0.027</td>
<td>1.12</td>
</tr>
<tr>
<td>BOYS$^{12}$</td>
<td>1</td>
<td>0.01</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**Equation 2.**

$$\sigma_{\text{gain}} = \beta \sigma_{\varepsilon}(\lambda) - (1-\beta) \sigma_{\varepsilon}(\lambda)$$

**Conclusion**

An original flux method was selected to obtain trivalent ytterbium doped LGOB single crystals. Luminescence spectra are reported in the near infrared spectral range. Absorption and emission cross sections of Yb-LGOB single crystals are reported for the first time and reflect interesting performances making this material a promising candidate for CW or pulsed laser sources.

**Acknowledgements**

This work has been supported by the Conseil Régional d’Aquitaine (contract N°20071101024) and the CNRS. Marie Chavoutier is the holder of a PhD thesis fellowship from the Conseil Régional d’Aquitaine.

Received: December 10, 2009.

---


The Solvent Free Melt Synthesis – A Way to Generate Highly Aggregated Systems with Promising Properties

A. Zurawski, C. J. Höller, J.-C. Rybak and K. Müller-Buschbaum*

Department of Chemistry and Biochemistry, Ludwig-Maximilians-Universität München, Butenandtstr. 5-13(D), 81377 München, Germany
E-mail: kmbch@cup.uni-muenchen.de

Abstract. Reactions of lanthanide metals with self-consuming amine melts of organic ligands can yield a large variety of rare earth amides and amine complexes. The absence of classic solvents directs the reactions towards aggregated systems like coordination polymers and frameworks even together with a high tendency for the formation of homoleptic products. As the absence of solvents does also include the absence of possible co-ligands that otherwise would fill the coordination sphere of the large rare earth ions, it generates reaction conditions that prove especially fruitful to obtain compounds free of unwanted co-ligands. Even more interesting this can go along with a variety of properties like luminescence, high thermal stability or porosity.

Keywords: Rare earth elements; Solvent free synthesis; Coordination polymers; Framework structures; MOFs

Introduction

In addition to cyclopentadienyl and complexes with oxygen containing ligands amides form the third pillar of rare earth metal coordination chemistry.¹

Solvent containing reaction routes dominate all fields thereof. Many compounds which were synthesized in this manner are solvates and are therefore heteroleptic unless the ligands are multi-chelating. Furthermore the co-coordination of solvent molecules mostly leads to the formation of small molecular units, such as monomers, dimers or oligomers. In order to avoid both heteroleptic products and small molecules we successfully elaborated solvent free melt syntheses including crystallization under melt conditions. Self-consuming amine melts oxidize rare earth metals at high temperatures concerning the organic ligands combined with an activation of the metals by catalytic amounts of mercury, micro waves or ammonia, yielding homoleptic amides and amine complexes.²

Discussion

The non-noble character of the lanthanides renders them highly reactive and relatively easy to oxidize. Even rather basic amines like nearly all aromatic N-heterocyclic amines can be used to produce hydrogen gas, trivalent and to some extent divalent rare earth ions. Starting from small molecular complexes like substituted pyrazolates³ that needed to be small in order to be re-crystallized from weakly coordinating solvents after the reaction with the amine melt, we developed this method to complete access to an entirely solvent-free procedure. Upon crystallization from the melt conditions highly aggregated systems became available. Depending on the

Ligands like carbazole or pyrazole\textsuperscript{4} strand like 1-D coordination polymers are formed that rely on a combination of $\sigma$-Ln-N bonds as well as $\pi$-aromatic-Ln bonds. Ligands like 1,2,3- and 1,2,4-triazole enable the formation of 2D-network structures and the very first 3D-Ln-N-MOFs \textsuperscript{5} (see Figure 1).

If imidazole is used the thermally most stable known MOFs known today can be achieved, which exhibit thermal endurance up to 650°C.\textsuperscript{6} The absence of solvents also promotes properties that are hindered by quenching groups and for which additional solvent molecules can also be less favourable like luminescence. E.g. the homoleptic MOF $\beta_{\alpha}$-[Tb(Im)$_3$]\textsuperscript{6} in addition to being the thermally most stable MOF framework exhibits bright green Tb\textsuperscript{3+} luminescence with a QE of 22%. This is remarkable as the rare earth ion and thus the number of luminescent centres is 100%, which is expected to show a significant quenching by concentration.

In all reactions the thermal parameter plays an important role. We have shown for pyrazole\textsuperscript{7} that it is likely that the reactions that end in the formation of coordination polymers start with small molecular units, usually from a monomeric complex that is rich on additionally coordinating molecules from the melt. Upon thermal treatment condensation steps occur. Under release of neutral equivalents of the melt ligands dimeric, then oligomeric complexes are formed prior to coordination polymers being extractable. For the ligand benzotriazole we could even show that stable crystalline polymeric strands of the formula $\alpha_{\alpha}$-[Ln(Btz)$_3$BtzH] can be transformed into 3D homoleptic MOFs of the formula $\beta_{\alpha}$-[Ln(Btz)$_3$].\textsuperscript{8}

![Diagram of coordination polymers and MOFs](image-url)

**Figure 1.** Crystal structures of the coordination polymers and MOFs $\alpha_{\alpha}$-[Ln(Cbz)$_3$] a), $\beta_{\alpha}$-[Ln(Pz)$_3$(PzH)$_3$] b), $\beta_{\alpha}$-[Ln(1,2,3-Tz)$_3$] c), $\beta_{\alpha}$-[Ln(1,2,4-Tz)$_3$(1,2,4-TzH)$_2$] 1,2,4-TzH d), $\beta_{\alpha}$-[Ln(1,2,4-Tz)$_3$] e), $\beta_{\alpha}$-[Ln(Im)$_3$] f), $\beta_{\alpha}$-[Ln(Btz)$_3$] g), $\beta_{\alpha}$-[Ln(Me$_4$BpzH)$_3$ (Me$_4$BpzH$_2$)] h) (from top left to bottom right).


These reactions are redox reactions and follow the equation:

\[ M + x R_2N \rightarrow [M(NR_2)_x] + \frac{1}{2} H_2 \]  (eq. 1)

In addition and for all ligands that do not provide an N-H group for the redox reaction or that have a N-H acidity being too low for this reaction, the metal side can be adjusted to already provide a suitable oxidation state. This can achieved e.g. by starting from anhydrous metal halides, which then react with N-donor melts, again without a classic solvent. According to this procedure a couple of MOFs could be obtained from 4,4'-bipyridine and the benzodinitriles 1,3- and 1,4-Ph(CN)₂.

\[ MX_y + x R \rightarrow [MX_y(NR_2)_x] \]  (eq. 2)

\[ MX_y + x R-CN \rightarrow [MX_y(NC-R)_x] \]  (eq. 3)

As another structure / property relation the formation of frameworks and Ln-N-MOFs is accompanied by the option to include porosity and thus to create porous hybrid materials from the solvent free reaction route (see Figure 2). For \( \infty [\text{Tb(Im)}_3] \), e.g. the accessible space in the structure regarding molecules of the size of a water molecule is about 10%. For \( \infty [\text{Ln(Im)}_3\text{ImH}] \) this can vary up to 26% of the volume of the structures. Also extended ligands like bipyrazolyle ligands can be successfully utilized like in \( \infty [\text{Eu(Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)] \)

Figure 2. The structure of the 2D-MOF \( \infty [\text{Tb}_2\text{Cl}_6(4,4\text{-Bipy})_3] \) as a depiction of the van-der-Waals spheres, N₂-BET sorption investigations indicating template removal and formation of a micro as well as mesoporous framework upon release of 2 eqv of 4,4-Bipy starting from the formula \( \infty [\text{Tb}_2\text{Cl}_6(4,4\text{-Bipy})_3](4,4\text{Bipy})_2 \), and microscopic photography of bright green luminescent single crystals of the MOF material.

Conclusion

As we present working without classic solvents is an alternative to solution chemistry directing products into the directions of homoleptic species as well as coordination polymers and frameworks. The synthesis strategy of using self consuming organic melts with no additional solvents thus proves a formidable way to generate highly aggregated systems with promising properties. High thermal stability, possible luminescence and porosity render these compounds attractive in multiple ways.

Acknowledgements

This work has been supported by the DFG within the SPP-1166 “Lanthanoid-spezifische Funktionalitäten” and SPP-1362 “MOFs” as well as the LMU Munich, the Wilhelm-Klemm and the Dr.-Otto-Röhm Foundations. We thank Dr. R. Köhn for help with the BET investigations.

Received: December 17, 2009.


Rare-Earth Metal(III) Chloride ortho-Oxomolybdates(VI): One Formula $\text{RECl}[\text{MoO}_4]$ ($\text{RE} = \text{Y, La} – \text{Nd, Sm} – \text{Lu}$) but Four Structure Types

Ingo Hartenbach*

Universität Stuttgart, Institut für Anorganische Chemie, Pfaffenwaldring 55, D-70569 Stuttgart, Germany
E-mail: hartenbach@iac.uni-stuttgart.de

Abstract. The structural family of rare-earth metal(III) chloride ortho-oxomolybdates(VI) with the formula $\text{RECl}[\text{MoO}_4]$ ($\text{RE} = \text{Y, La} – \text{Nd, Sm} – \text{Lu}$) occurs in four different crystal structures, depending on the size of the $\text{RE}^{3+}$ cation. The larger ones (La, Ce, and Pr) crystallize pseudo-orthorhombically in the monoclinic space group $C2/c$, usually showing twinning. Besides a coordination environment of six $O^{2–}$ anions, the rare-earth metal cations are surrounded by two $\text{Cl}^{–}$ anions, although both of them show a coordination number of two. While (Cl1)$^+$ anions emerge as isolated tetrahedral $[\text{MoO}_4]^{2–}$ units. The most peculiar building blocks in this structure, however, are provided by the chloride anions, although both of them show a coordination number of two. While (Cl1)$^+$ forms an isolated rhombus-shaped unit of the formula $[(\text{Cl1})_4(\text{Nd1})_4]^{14+}$, the (Cl2)$^–$ anions build up a chain along [010] according to $\frac{1}{2} [(\text{Cl2})_4(\text{Nd2})_4]^{22–}$. NdCl[MoO4] shows a unique structural setup (orthorhombic, space group $Pbam$) within the $\text{RECl}[^{+1}\text{MoO}_4]$ series. Its two crystallographically independent Nd$^{3+}$ cations show a coordination number of eight only, and are surrounded in the shape of distorted trigonal dodecahedra built of two $\text{Cl}^{–}$ and six $O^{2–}$ anions. The molybdate units emerge as isolated tetrahedral $[\text{MoO}_4]^{2–}$ units. The most peculiar building blocks in this structure, however, are provided by the chloride anions, although both of them show a coordination number of two. While (Cl1)$^+$ forms an isolated rhombus-shaped unit of the formula $[(\text{Cl1})_4(\text{Nd1})_4]^{14+}$, the (Cl2)$^–$ anions build up a chain along [010] according to $\frac{1}{2} [(\text{Cl2})_4(\text{Nd2})_4]^{22–}$. This chain is no longer observed in the crystal structures of the smaller lanthanides ($\text{RE} = \text{Y, Sm} – \text{Yb}$), which crystallize monoclinically in space group $C2/m$ and consist of the afore-mentioned $[(\text{Cl1})_4(\text{Nd1})_4]^{14+}$ rhombi as the only building block observed for the chloride anions. Again, the rare-earth metal cations are surrounded by two $\text{Cl}^{–}$ and six $O^{2–}$ anions to form distorted trigonal dodecahedra and, furthermore, isolated $[\text{MoO}_4]^{2–}$ tetrahedra are present in the crystal structure. Finally, LuCl[MoO4] crystallizes triclinically in space group $\overline{P}T$. Due to the smaller ionic radius of the Lu$^{3+}$ cations their coordination number is reduced to seven in the shape of a monocapped trigonal prism formed by two $\text{Cl}^{–}$ and five $O^{2–}$ anions. However, no difference to $\text{RECl}[\text{MoO}_4] (\text{RE} = \text{Sm} – \text{Yb})$ is observed considering the isolated $[\text{MoO}_4]^{2–}$ anions and the $[\text{Cl}_3\text{Lu}_3]^{30+}$ rhombi.

Keywords: Rare-Earth Elements; Solid State Chemistry; Structure; Luminescence

Introduction

In times of global warming the quest for efficient energy saving materials is more important than ever. One of those special tasks is the synthesis and analysis of luminescent materials. Derivatives of rare-earth metal oxomolybdates come into focus, since they are able to provide both, host positions for cationic doping with luminescent-active lanthanoid cations (e.g. Eu$^{3+}$, Tb$^{3+}$, etc.) and with the LMCT-active anion $[\text{MoO}_4]^{2–}$ a chance for excitation in a broad energy range, a so-called inorganic antenna effect. One approach, to the topic is the work with derivatizing anions, such as halides. Preliminary work comprises the preparation of rare-earth metal(III) fluoride oxomolybdates(IV) of the formula $\text{REF}[\text{MoO}_4] (\text{RE} = \text{Y}^3$, Sm – Tm$^3$) of which the yttrium compound has proven to be a suitable host material for doping with luminescence-active trivalent lanthanoid cations. In case of the larger rare-earth metal cations a different, fluoride poorer composition is realized with

The latter is also suitable for doping to obtain luminescence properties. In contrast, one formula type, $\text{RECl}[\text{MoO}_4]$ is realized for the complete lanthanide series if fluoride is replaced by the larger chloride anions, but four structure types are observed, depending on the size of the rare-earth metal trication.

**The $\text{RECl}[\text{MoO}_4]$ structure as observed for the larger lanthanides ($\text{RE} = \text{La, Ce, Pr}$)**

The $\text{RECl}[\text{MoO}_4]$ series of the larger lanthanides ($\text{RE} = \text{La, Ce, Pr}$) crystallizes pseudo-orthorhombically in the monoclinic space group $\text{P}\overline{2}_1/c$ with eight formula units per unit cell and lattice parameters according to Table 1.

<table>
<thead>
<tr>
<th>$\text{RECl}[\text{MoO}_4]$</th>
<th>$a$ / pm</th>
<th>$b$ / pm</th>
<th>$c$ / pm</th>
<th>$\beta$ / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl[MoO$_4$]</td>
<td>1920.55(18)</td>
<td>580.46(5)</td>
<td>803.82(7)</td>
<td>90.040(6)</td>
</tr>
<tr>
<td>CeCl[MoO$_4$]</td>
<td>1912.38(18)</td>
<td>579.92(5)</td>
<td>795.91(7)</td>
<td>90.037(6)</td>
</tr>
<tr>
<td>PrCl[MoO$_4$]</td>
<td>1906.31(18)</td>
<td>579.68(6)</td>
<td>788.86(7)</td>
<td>90.036(6)</td>
</tr>
</tbody>
</table>

The crystal structure comprises two crystallographically different ions of any sort, which is owed to the pseudo-orthorhombicity. The rare-earth metal cations are surrounded by six $\text{O}^{2-}$ and three plus one $\text{Cl}^-$ anions (CN = $9+1$) in the shape of tetracapped trigonal prisms (Fig. 1, top left). The $\text{Mo}^{6+}$ cations are basically surrounded by four $\text{O}^{2-}$ anions in distances of 170 – 180 pm, which are rather usual for tetrahedral $[\text{MoO}_4]^{2-}$ units. However, a fifth $\text{O}^{2-}$ anion in a distance of about 235 pm is found in the vicinity of $\text{Mo}^{6+}$, therefore its coordination environment is better described as a trigonal bipyramid (= two face shared tetrahedra) with the central molybdenum cation situated in one of the two partial tetrahedra (Fig. 1, top right). These trigonal bipyramids are fused together via common apical vertices $\text{\{[MoO}_{4/3}(\text{v})\text{O}_{1/3}(\text{t})]\}^2$ (v = vertex-connecting, t = terminal) to form strands along [001] (Fig. 2). The $\text{Cl}^-$ anions are surrounded by three plus one lanthanide cations in the shape of distorted tetrahedra which are connected to each other by four common edges building up a layer according to $\text{\{[ClRE}_{3}^{13/13,1}^{2+}\}}$ (e = edge-connecting) analogous to the sheets in a very distorted litharge-type $\text{PbO}^5$ (Fig. 1, bottom).

**Figure 1.** Coordination environment around the $\text{RE}^{3+}$ cations (top left) and the $\text{Mo}^{6+}$ cations (bottom left) as well as the $\text{\{[ClRE}_{3}^{13/13,1}^{2+}\}}$ layer (right) in the crystal structure of $\text{RECl}[\text{MoO}_4]$ ($\text{RE} = \text{La, Ce, Pr}$).
The $\ldots$ layers and $\ldots$ strands built up the crystal structure by being alternately piled along [100]. At first glance of the unit cell the $a$ axis could be sufficient with half its length. Although, as seen in Fig. 2, the Mo$^{6+}$ cations in the left part of the cell are situated in the lower partial tetrahedra of the trigonal bipyramids, while those in the right part of the cell reside in the upper partial tetrahedra. Thus, the $a$ axis has to be two times the length needed for one piled unit.

Due to the peculiar arrangement of the rare-earth metal cations in a litharge analogous layer a special magnetic behaviour as e.g. found in $RE_2O_4Se[Se_2]$ was assumed. However, besides a small ferromagnetic effect discovered in the magnetic measurements of CeCl[MoO$_4$], usual Curie-Weiss behaviour is observed (Fig. 3).

---

**Figure 2:** View at the unit cell of $RECl[MoO_4]$ ($RE = La, Ce, Pr$) along [010].

**Figure 3:** Magnetic susceptibility measurement of CeCl[MoO$_4$]

---

The crystal structure of NdCl[MoO₄]³⁺

Very often in a series of rare-earth metal(III) compounds, the neodymium derivative crystallizes isostructural to the representatives of the larger cations (RE = La – Pr), less often to structures accommodating the smaller cations (RE = Sm – Lu). In case of the rare-earth metal(III) chloride ortho-oxomolybdates(VI), however, the neodymium compound exhibits a unique crystal structure, which is not isotypic to any other representative of this family. NdCl[MoO₄] crystallizes orthorhombically in space group Pbam \( (a = 1991.61(9) \text{ pm}, b = 693.79(3) \text{ pm}, c = 742.53(3) \text{ pm}) \) with eight formula units per unit cell. Both crystallographically independent Nd³⁺ cations are situated in the voids of this network, forming [MoO₄]²⁻ anions built up zig-zag chains (Fig. 4, second left). Furthermore, two crystallographically distinguishable chloride anions are found in the crystal structure, which both show a coordination number of two. While in case of Cl1 an isolated, planar, rhombus-shaped unit according to \([\text{Cl}_1]_2(\text{Nd}_1)_2]^{\text{4+}}\) is formed (Fig. 4, bottom right), the (Cl₂⁻) anions built up zig-zag chains of the Niggli formula \(\downarrow [(\text{Cl}_2)(\text{Nd}_2)]^{\text{4+}}\) along the b axis (Fig. 4, top right).

![Figure 4](image_url)

**Figure 4.** Basic building blocks in the crystal structure of NdCl[MoO₄]: coordination polyhedron around the Nd³⁺ cations (left), anionic environment around the [MoO₄]²⁻ tetrahedra (second left), [(Cl1)₂(Nd1)₂]⁴⁺ rhombus (bottom right) and \(\downarrow [(\text{Cl}_2)(\text{Nd}_2)]^{\text{4+}}\) zig-zag chain (top right).

There are two possibilities to describe the three-dimensional arrangement of the crystal structure. Considering the [NdCl₂O₄]¹⁺ polyhedra as building blocks, those around Nd1 and Nd2 are alternately fused together by common oxygen edges to form chains along [001]. These chains further connect to double chains via common edges at Cl1, hence the [(Cl1)₂(Nd1)₂]⁴⁺ rhombi emerge. These double chains are now interconnected to each other by common Cl2 vertices (\(\downarrow [(\text{Cl}_2)(\text{Nd}_2)]^{\text{2+}}\) zig-zag chains are built) to form a network according to \(\downarrow [\text{Nd}_2\text{O}_5\text{S}_2\text{O}_{14}, (\text{Cl}_1)_{\text{v}_{\text{e}}}, (\text{Cl}_2)_{\text{v}_{\text{e}}}, (\text{Cl}_2)_{\text{v}_{\text{e}}}^{\text{12}}]^{\text{12+}}\) (\(t = \text{terminal}, v = \text{vertex-connecting}, e = \text{edge-connecting}\)). Finally, the Mo⁶⁺ cations are situated in the voids of this network, forming [MoO₄]²⁻ tetrahedra. The second way to describe the structural setup of NdCl[MoO₄] is to use the [(Cl1)₂(Nd1)₂]⁴⁺ rhombi and the \(\downarrow [(\text{Cl}_2)(\text{Nd}_2)]^{\text{2+}}\) zig-zag chains as cationic and the isolated [MoO₄]²⁻ tetrahedra as anionic building blocks. All these blocks are aligned or run along the b axis, respectively. The isolated rhombus shaped [(Cl1)₂(Nd1)₂]⁴⁺ units are thereby situated with their centres at (0,0,0) and \((1/2,1/2,0)\) while the \(\downarrow [(\text{Cl}_2)(\text{Nd}_2)]^{\text{2+}}\) zig-zag chains run along \([1/4, y, 1/2]\) (and \([1/4, y, 1/2]\)) thus a tetragonal rod-like packing of the cationic building blocks forms. The interstices of this packing are also arranged according to a tetragonal rod-packing and are filled with the anionic [MoO₄]²⁻ tetrahedra, which are pearl-chain like piled along [010] (Fig. 5). Although, this structure represents a unique setup in the RECl[MoO₄] series, certain similarities with the crystal structure of the smaller representatives, which are described in the next chapter, can be detected.

---


© 2010 NWT-Verlag, Bornheim, Germany
The \( \text{RECl}[\text{MoO}_4] \) structure as observed for the smaller rare-earth metals (\( \text{RE} = \text{Y, Sm – Lu} \))

The crystal structure of \( \text{RECl}[\text{MoO}_4] \) comprising the smaller rare-earth metals (\( \text{RE} = \text{Y, Sm – Yb} \)) was determined to be monoclinic (space group \( \text{C}2/m \)) with lattice constants according to Table 2 and four formula units per unit cell.

Table 2. Lattice constants for \( \text{RECl}[\text{MoO}_4] \) (\( \text{RE} = \text{Y, Sm – Yb} \))

<table>
<thead>
<tr>
<th></th>
<th>( a ) / pm</th>
<th>( b ) / pm</th>
<th>( c ) / pm</th>
<th>( \beta ) / deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{YCl}[\text{MoO}_4] )</td>
<td>1019.02(5)</td>
<td>720.67(4)</td>
<td>681.50(3)</td>
<td>107.130(4)</td>
</tr>
<tr>
<td>( \text{SmCl}[\text{MoO}_4] )</td>
<td>1034.80(5)</td>
<td>736.02(4)</td>
<td>690.84(3)</td>
<td>106.677(2)</td>
</tr>
<tr>
<td>( \text{EuCl}[\text{MoO}_4] )</td>
<td>1031.61(5)</td>
<td>732.80(3)</td>
<td>688.78(3)</td>
<td>106.773(2)</td>
</tr>
<tr>
<td>( \text{GdCl}[\text{MoO}_4] )</td>
<td>1028.90(5)</td>
<td>730.51(3)</td>
<td>687.11(3)</td>
<td>106.864(2)</td>
</tr>
<tr>
<td>( \text{TbCl}[\text{MoO}_4] )</td>
<td>1025.17(5)</td>
<td>726.82(3)</td>
<td>684.97(3)</td>
<td>106.963(2)</td>
</tr>
<tr>
<td>( \text{DyCl}[\text{MoO}_4] )</td>
<td>1021.99(5)</td>
<td>723.67(3)</td>
<td>683.22(3)</td>
<td>107.057(2)</td>
</tr>
<tr>
<td>( \text{HoCl}[\text{MoO}_4] )</td>
<td>1019.00(5)</td>
<td>721.47(3)</td>
<td>681.48(3)</td>
<td>107.142(2)</td>
</tr>
<tr>
<td>( \text{ErCl}[\text{MoO}_4] )</td>
<td>1015.36(5)</td>
<td>718.74(3)</td>
<td>679.64(3)</td>
<td>107.236(2)</td>
</tr>
<tr>
<td>( \text{TmCl}[\text{MoO}_4] )</td>
<td>1013.36(5)</td>
<td>715.91(3)</td>
<td>678.50(3)</td>
<td>107.320(2)</td>
</tr>
<tr>
<td>( \text{YbCl}[\text{MoO}_4] )</td>
<td>1010.27(5)</td>
<td>713.34(3)</td>
<td>677.56(3)</td>
<td>107.408(2)</td>
</tr>
</tbody>
</table>

However, the lutetium compound is no longer able to maintain this structure, and therefore \( \text{LuCl}[\text{MoO}_4] \) crystallizes triclinically in space group \( \text{P}T \) (\( a = 591.42(2) \) pm, \( b = 716.19(3) \) pm, \( c = 681.44(3) \) pm, \( \alpha = 93.724(2)^\circ, \beta = 102.463(2)^\circ, \gamma = 122.134(2)^\circ, Z = 2 \)) which establishes a direct group-subgroup relationship between the two unit cells. This is especially obvious in the surrounding of the chloride and the molybdate anions. In both structures isolated planar rhombus-shaped \( \text{[Cl}_2\text{RE}^2]^4^+ \) units represent the chloride surrounding (Fig. 6, middle). The isolated tetrahedral \( \text{[MoO}_4]^2^- \) entities are surrounded by five rare-earth metal trications which all arrange terminal in case of triclinic \( \text{LuCl}[\text{MoO}_4] \) (Fig. 6, bottom right). In the monoclinic \( \text{RECl}[\text{MoO}_4] \) (\( \text{RE} = \text{Sm – Yb} \)) series only four of the \( \text{RE}^{3+} \) cations coordinate terminal at the oxomolybdate unit, while the fifth one is edge-capping (Fig. 6, top right). Hence, the two coordinately effective distances of the edge-capping \( \text{RE}^{3+} \) cations range both between 256 and 261 pm. These distances unite in \( \text{LuCl}[\text{MoO}_4] \) to form a short, coordinating one at 237 pm and a long one at about 310 pm (represented as dashed bond in Fig. 6, bottom right).

---

The consequence of this behaviour is a reduction in the coordination number of the rare-earth metal trication from eight in the monoclinic structure type of the \( \text{RECl}[\text{MoO}_4] \) series with the anions building up a trigonal dodecahedron around the rare-earth metal trication (Fig. 6, top left) to seven in the triclinic structure of the lutetium derivative, in which a monocapped trigonal prism (Fig. 6, bottom left) is formed.

**Figure 6.** Coordination environment around the rare-earth metal cations (left) and the ortho-oxomolybdate anions (right) in monoclinic \( \text{RECl}[\text{MoO}_4] \) \((\text{RE} = \text{Sm} – \text{Yb}, \text{top})\) and triclinic \( \text{LuCl}[\text{MoO}_4] \) (bottom). The planar \([\text{Cl}_2\text{RE}_2\text{O}_6]^4–\) rhombi (middle) are equal in both structure types.

The trigonal \([\text{RECl}_2\text{O}_8]\) dodecahedra in the monoclinic \( \text{RECl}[\text{MoO}_4] \) representatives \((\text{RE} = \text{Sm} – \text{Yb})\) are fused together via three common edges to form a layer according to \( \frac{1}{2}[\text{RECl}_{2\frac{1}{2}}\text{O}_{4\frac{1}{2}}\text{O}_{1\frac{1}{2}}]^6–\) parallel (110). Since, there is one fewer ligand around the \( \text{Lu}^{3+} \) cations in triclinic \( \text{LuCl}[\text{MoO}_4] \), the dimensionality of their interconnection is reduced by one and thus, chains of the composition \( \frac{1}{2}[\text{LuCl}_{2\frac{1}{2}}\text{O}_{4\frac{1}{2}}\text{O}_{1\frac{1}{3}}]^6–\) along [100] are formed. Considering the anionic \([\text{MoO}_4]^{2–}\) tetrahedra and the cationic \([\text{Cl}_3\text{RE}_2]^{4+}\) units as building blocks of the crystal structure both the monoclinic and the triclinic setup are rather similar. In both structures these building blocks are aligned along the c axis and thus form a tetragonal rod packing (Fig. 7)

**Figure 7.** View at the crystal structures of monoclinic \( \text{RECl}[\text{MoO}_4] \) \((\text{RE} = \text{Sm} – \text{Yb}, \text{top})\) and triclinic \( \text{LuCl}[\text{MoO}_4] \) (bottom) along [001] in both cases.

© 2010 NWT-Verlag, Bornheim, Germany
So far, it was not possible to dope the "innocent" host lattice YCl[MoO₄] with Eu³⁺ or Tb³⁺ cations to obtain luminescent materials. But surprisingly, the bulk materials of EuCl[MoO₄] and TbCl[MoO₄] show red and green luminescence, respectively, when excited with a UV lamp (Fig. 8). Luminescence spectroscopy was performed with both compounds which showed that concentration quenching, as expected, is almost not present in those derivatives.

![Figure 8. Red luminescence of bulk EuCl[MoO₄] (left) and green luminescence of bulk TbCl[MoO₄] (right) under UV excitation.](image)

**Experimental.** The title compounds are synthesized by fusing the respective rare-earth metal sesquioxide (RE₂O₃, 99.9%; ChemPur, Karlsruhe, Germany) and rare-earth metal trichloride (RECl₃, 99.9%; ChemPur, Karlsruhe, Germany) together with molybdenum trioxide (MoO₃, p. a., Merck, Darmstadt, Germany) in a molar ratio of 1:1:3 in evacuated silica ampoules for seven days at 900 °C (for RE = La, Ce, Pr) or 850 °C (for RE = Y, Nd, Sm – Lu). All products emerge phase-pure according to powder X-ray diffractometry, as bulky single crystals which remain stable to air and water, showing the colour of the respective rare-earth metal trication.

**Crystal structures.** Single crystals were selected under a microscope and sealed in thin-walled glass capillaries. Intensity data sets were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo-Kα radiation. Details of the crystal structure investigations are available from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +497247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-420980 for LaCl[MoO₄], CSD-420981 for CeCl[MoO₄], CSD-420982 for PrCl[MoO₄], CSD-420360 for NdCl[MoO₄], CSD-420058 for SmCl[MoO₄], CSD-420054 for EuCl[MoO₄], CSD-420055 for GdCl[MoO₄], CSD-420059 for TbCl[MoO₄], CSD-420052 for DyCl[MoO₄], CSD-420056 for HoCl[MoO₄], CSD-420053 for ErCl[MoO₄], CSD-420060 for TmCl[MoO₄], CSD-420061 for YbCl[MoO₄], and CSD-420057 for LuCl[MoO₄].

**Acknowledgements.**

The graduate students Andreas Bogner and Florian Ledderboge are acknowledged for preparing the title compounds as part of their advanced and applied laboratory course in inorganic chemistry. Furthermore, I thank Prof. Dr. Thomas Schleid for allowing me to follow my own ideas with his resources and Dr. Sabine Strobel for valuable discussions. Magnetic measurements were carried out at Colorado State University, Fort Collins, CO, USA under the supervision of Prof. Dr. Peter K. Dorhout.

Received, December 18, 2009.
Structure Optimization and Electronic Structure of the SrAl$_2$O$_4$:Eu$^{2+}$ Persistent Luminescence Material by DFT Calculations

Jorma Hölsä$^{1,2}$, Taneli Laamanen$^{1,3,*}$, Mika Lastusaari$^{1,2}$, Pavel Novák$^4$

$^1$ University of Turku, Department of Chemistry, FI-20014 Turku, Finland
$^2$ Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland
$^3$ Graduate School of Materials Research (GSMR), Turku, Finland
$^4$ Academy of Sciences of the Czech Republic, Institute of Physics, CZ-16253 Prague 6, Czech Republic
E-mail: taneli.laamanen@utu.fi

Abstract. The electronic and crystal structure of the non-optimized and optimized Eu$^{2+}$ doped strontium aluminate (SrAl$_2$O$_4$:Eu$^{2+}$) material was studied by using the density functional theory (DFT) calculations. The calculations were focused to probe the changes in the local environment and electronic structure of the Eu$^{2+}$ ion in the two Sr sites. The introduction of the Eu$^{2+}$ ion induced minor structural modifications of the environment of the Eu$^{2+}$ luminescent center when the structure was optimized. The resulting increase in the electron repulsion shifted the Eu$^{2+}$ 4f$^7$ ground state slightly higher in the energy gap of SrAl$_2$O$_4$. Accordingly, the two band luminescence shown by Eu$^{2+}$ at low temperatures is suggested to originate rather from the excited 4f$^6$5d$^1$ states than from different sites.

Keywords: Strontium aluminate; Europium; Persistent luminescence; Electronic structure; Density functional theory calculation

Introduction

The search for novel thermally stimulated luminescence materials has been hindered by the trial and error methods used due to the limited knowledge about the energy storage mechanisms in the aluminate materials. The systematic investigations demand the exact knowledge of the luminescence mechanisms and the trap identification. The alkaline earth aluminites (MAI$_2$O$_4$: RE$^{3+}$, M: Ca, Sr and Ba) doped with Eu$^{2+}$ and co-doped with selected rare earth (R$^{3+}$) ions as Dy$^{3+}$ and Nd$^{3+}$, are efficient blue/green emitting persistent luminescence materials e.g. in luminous paints$^1$-$^3$. The proposed persistent luminescence mechanisms$^4$-$^5$ have not yet been thoroughly proven since essential experimental data is missing or contradictory. The connection between the electronic band structure of the host as well as the energy levels of intrinsic lattice defects (vacancies, interstitials etc.) and the rare earth (co-)dopants needs to be clarified to fully understand the energy storage properties of the persistent luminescence materials.

The effect of the local environment of the luminescent center on the optical properties of the oxidic persistent luminescence materials is currently not well understood. The inclusion of the Eu$^{2+}$ ion and/or intrinsic lattice defects in the persistent luminescence materials may create locally important modifications into the host structure. Possible modifications in the local electronic structure should not be overlooked either since even small changes in the electronic structure may have a significant effect on the persistent luminescence efficiency. The energy storage properties of the persistent luminescence materials can be fully understood only by combining theoretical methods with experimental studies. This kind of sophisticated approach is urgently needed to enable systematic development of new efficient materials.

---

In this work, the electronic structure of the Eu\(^{2+}\) doped strontium aluminate (SrAl\(_2\)O\(_4\):Eu\(^{2+}\)) material was studied with density functional theory (DFT) calculations. The changes in the local environment of Eu\(^{2+}\) as well as in the electronic structure due to the optimization of the crystal structure were studied, too.

Results and discussion

Structure optimization. All the SrAl\(_2\)O\(_4\) materials studied possess the monoclinic structure\(^6\) (space group: P\(_2_1\), no. 4, Z: 4, a = 8.447, b = 8.816, c = 5.163 Å and \(\beta = 93.4^\circ\)). The structure consists of Sr\(^{2+}\) ions situated within channels formed by interconnected AlO\(_4\) tetrahedra. No non-bridging (with Al) oxide ions exist in the structure. The structure possesses two Sr and eight O sites. The Eu\(^{2+}\) ion is expected to substitute for Sr\(^{2+}\) in both sites (Sr1 and Sr2) present in the SrAl\(_2\)O\(_4\) host, since the respective Sr-O distances are very similar for both sites (Table 1). The statistical ionic radii of the seven coordinated species of Eu\(^{2+}\) (1.20 Å) and Sr\(^{2+}\) (1.21 Å) are close to a perfect match\(^7\). In contrast, Eu\(^{2+}\) does not fit at all into the small four coordinated Al\(^{3+}\) site (0.39 Å). The DFT calculations including the Eu\(^{2+}\) ion were carried out using a normal unit cell (Z: 4). One of the four Sr\(^{2+}\) ions in the unit cell was replaced by Eu\(^{2+}\) corresponding to a rather high (25 %) activator ion concentration in the material. The Eu\(^{2+}\) ion was placed into either the Sr1 or Sr2 site. The experimental Eu\(^{2+}\) concentration (1 %) is significantly lower and the high Eu\(^{2+}\) concentration was used here to probe the local modifications in the crystal and electronic structure induced by the introduction of the Eu\(^{2+}\) ion.

The Eu-O and Sr1-O (Sr2-O) distances were found equal in the non-optimized structure (Table 1). Due to structure optimization, the distances between the Sr\(^{2+}\) and Eu\(^{2+}\) ions and the nearest oxide ions are decreased, though some distances are increased slightly, too. The average change in the Sr(Eu)-O distance is 0.021-0.038 Å. The differences in changes between the Sr1 and Sr2 sites are almost negligible. The decrease in the Sr-O and Eu-O distances takes place at the expense of lengthening Al-O distances, in average increased by 0.017 Å. The average changes relative to the non-optimized distances (Sr-O: 2.69 (Sr1) and 2.67 Å (Sr2), Al-O: 1.75 Å) are thus almost similar for Sr(Eu)-O and Al-O, 0.8-1.4 and 1.0 %, respectively. In the Sr1 site, two types of oxide ion movement – changes in both the O-Eu-O angle and the Eu-O distance – exist due to optimization (Fig. 1).

The slight change in the total energy from the non-optimized to the optimized structure of the Eu\(^{2+}\) doped SrAl\(_2\)O\(_4\) (from -640554.32 to -640554.49 eV) reflects the small changes in the atomic positions. The differences between the non-optimized and optimized crystal structure are small, although even smaller changes might be expected due to the almost similar statistical ionic radii of the Eu\(^{2+}\) and Sr\(^{2+}\) ions. Since the tabulated ionic radii are statistical ones, the actual inter-atomic distances may differ in individual materials, however.

![Environment of Eu\(^{2+}\) in the Sr1 site of SrAl\(_2\)O\(_4\):Eu\(^{2+}\). Non-optimized ion positions are marked with dashed spheres.](image)

---


Table 1. Distances between the Sr\(^{2+}\) (Eu\(^{2+}\)) and the nearest oxide ions in the optimized and non-optimized crystal structure of SrAl\(_2\)O\(_4\):Eu\(^{2+}\).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ion in Sr1 site</th>
<th>Distance to / Å</th>
<th>Difference* / Å</th>
<th>Ion in Sr2 site</th>
<th>Distance to / Å</th>
<th>Difference* / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-optimized</td>
<td>Sr / Eu</td>
<td>O3</td>
<td>2.521</td>
<td>Sr / Eu</td>
<td>O5</td>
<td>2.508</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O4</td>
<td>2.560</td>
<td>O8</td>
<td>2.536</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O7</td>
<td>2.572</td>
<td>O6</td>
<td>2.557</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O1</td>
<td>2.667</td>
<td>O4</td>
<td>2.609</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O2</td>
<td>2.677</td>
<td>O2</td>
<td>2.697</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O7</td>
<td>2.732</td>
<td>O1</td>
<td>2.773</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O6</td>
<td>3.113</td>
<td>O8</td>
<td>2.991</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>2.692</td>
<td>Average</td>
<td>2.667</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optimized</td>
<td>Sr</td>
<td>O3</td>
<td>2.510</td>
<td>Sr</td>
<td>O5</td>
<td>2.487</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O4</td>
<td>2.511</td>
<td>O8</td>
<td>2.504</td>
<td>-0.032</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O7</td>
<td>2.588</td>
<td>O6</td>
<td>2.526</td>
<td>-0.031</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O1</td>
<td>2.631</td>
<td>O4</td>
<td>2.602</td>
<td>-0.007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O2</td>
<td>2.609</td>
<td>O2</td>
<td>2.689</td>
<td>-0.008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O7</td>
<td>2.717</td>
<td>O1</td>
<td>2.737</td>
<td>-0.036</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O6</td>
<td>3.122</td>
<td>O8</td>
<td>3.005</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>Average (change)</td>
<td>2.670</td>
<td>0.029</td>
<td>Average (change)</td>
<td>2.650</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>Eu</td>
<td>O3</td>
<td>2.491</td>
<td>Eu</td>
<td>O5</td>
<td>2.470</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O4</td>
<td>2.516</td>
<td>O8</td>
<td>2.496</td>
<td>-0.040</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O7</td>
<td>2.559</td>
<td>O6</td>
<td>2.504</td>
<td>-0.053</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O2</td>
<td>2.622</td>
<td>O4</td>
<td>2.595</td>
<td>-0.014</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O1</td>
<td>2.608</td>
<td>O2</td>
<td>2.704</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O7</td>
<td>2.677</td>
<td>O1</td>
<td>2.754</td>
<td>-0.019</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O6</td>
<td>3.123</td>
<td>O8</td>
<td>3.012</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>Average (change)</td>
<td>2.656</td>
<td>0.038</td>
<td>Average (change)</td>
<td>2.648</td>
<td>0.027</td>
</tr>
</tbody>
</table>

* Difference to the non-optimized structure.

Electronic structure. The calculated band gap energy (\(E_g\); 6.4 eV) of SrAl\(_2\)O\(_4\):Eu\(^{2+}\) did not change whether the optimized or non-optimized crystal structures were used (for further discussion, cf. ref. 8). The agreement between the experimental (6.6 eV)\(^8\) and calculated values is very good and the difference of 0.2 eV is insignificant. This shows a considerable improvement to an earlier theoretical GGA approach\(^9\), where a largely underestimated \(E_g\) value of 4.5 eV was reported for SrAl\(_2\)O\(_4\). The derivative curves of both the excitation spectrum and the calculated total DOS were used to obtain accurate and comparable \(E_g\) values.

The position of the Eu\(^{2+}\) 4f\(^7\)S\(_{7/2}\) ground state is inside the energy gap of the SrAl\(_2\)O\(_4\) host. The ground state is located at 0.25 (Sr1 site) and 0.16 eV higher energy in the optimized structure compared to the non-optimized structure (Fig. 2). The change in the location of the 4f\(^7\) ground state is possibly due to the shorter Eu-O distances (cf. previous chapter), which results in a decrease in the expansion of the Eu\(^{2+}\) valence orbitals - including the 4f orbital. This results in an increase in the electron repulsion shifting the Eu\(^{2+}\) 4f\(^7\) ground state higher in the energy gap.

The luminescence spectrum of SrAl\(_2\)O\(_4\):Eu\(^{2+}\) due to the 4f\(^6\)5d\(^1\)(D) \(\rightarrow\) 4f\(^8\)(S\(_{7/2}\)) transitions of the Eu\(^{2+}\) ion consists of two bands centered at 445 and 520 nm (2.79 and 2.38 eV, respectively) at low temperature (20 K)\(^10\). Only one band at 520 nm is observed at room temperature. The two-band luminescence of SrAl\(_2\)O\(_4\):Eu\(^{2+}\) could most readily be explained by a corresponding difference in the position of the Eu\(^{2+}\) 4f\(^7\) ground state between the two Sr sites. The DFT calculations provide an excellent method to probe the changes of the 4f\(^7\) ground state of

---

the Eu\(^{2+}\) ion located in the Sr1 and Sr2 sites at low temperature since all the calculations correspond to low temperature (0 K) conditions. However, the calculated position of the 4f\(^6\) ground state of Eu\(^{2+}\) in the optimized Sr2 site was found at only slightly (0.09 eV) higher energy compared to Eu\(^{2+}\) in the optimized Sr1 site (Fig. 3). Therefore, the slight change in the Coulombic electron repulsion cannot explain the significant energy difference of 0.41 eV between the two luminescence bands.

Figure 2. Calculated density of states of the non-optimized and optimized SrAl\(_2\)O\(_4\):Eu\(^{2+}\) with Eu\(^{2+}\) located in the Sr1 site (GGA+U method, Hubbard parameter U: 7.62 eV, spin-orbit coupling not included).

Figure 3. Calculated density of states of the optimized SrAl\(_2\)O\(_4\):Eu\(^{2+}\) with Eu\(^{2+}\) located in the Sr1 and Sr2 site (GGA+U, U: 7.62 eV, spin-orbit coupling not included).

Luminescence is usually observed only from the lowest Eu\(^{2+}\) 4f\(^6\)5d\(^1\) state since the excited states are easily relaxed to the lowest 4f\(^6\)5d\(^1\) state located below the bottom of the conduction band. However, luminescence from a higher Eu\(^{2+}\) 4f\(^6\)5d\(^1\) state may be observed due to the absence of high energy lattice vibrations at low temperature. Luminescence from a higher Tm\(^{3+}\) 4f\(^{12}\)5d\(^1\) state has been reported\(^{11,12}\) and the Eu\(^{2+}\) ion may exhibit the same kind of unusual low temperature luminescence. The calculated density of the 4f\(^6\)5d\(^1\) states (Fig. 4) shows more than one 4f\(^6\)5d\(^1\) state below the conduction band which is a requirement essential for luminescence to be observed from a higher Eu\(^{2+}\) 5d state. Furthermore, the density of the 4f\(^6\)5d\(^1\) state located slightly below the conduction band edge at 6.4-6.5 eV is significantly higher compared to the lowest 4f\(^6\)5d\(^1\) state located at ca. 6 eV. The energy difference between these 4f\(^6\)5d\(^1\) states corresponds very well to the experimentally observed energy difference of 0.41 eV between the luminescence bands. Luminescence may therefore be observed from both the lowest (corresponding to \(\lambda_{\text{em}}\): 520 nm) and higher (445 nm) 4f\(^6\)5d\(^1\) state at low temperature resulting in


two luminescence bands (Fig. 5). However, only one luminescence band is observed at room temperature due to the fast relaxation of the system to the lowest $4f^65d^1$ state.

The presence of defects and defect aggregates close to the luminescent Eu$^{2+}$ center may have a significant effect on the luminescence properties of SrAl$_2$O$_4$:Eu$^{2+}$. These effects and their temperature dependence have to be studied in detail since they may provide further insight into the observed low temperature luminescence properties. This will be a subject of future work.

![Figure 4](image1.png)

**Figure 4.** Calculated density of the Eu$^{2+}$ $4f^65d^1$ states of the optimized SrAl$_2$O$_4$:Eu$^{2+}$ with Eu$^{2+}$ located in the Sr1 and Sr2 site (GGA+U, $U$: 7.62 eV, spin-orbit coupling not included).

![Figure 5](image2.png)

**Figure 5.** Luminescence processes of SrAl$_2$O$_4$:Eu$^{2+}$ at 20 and 295 K.

**Conclusions**

Changes in the environment of the Eu$^{2+}$ ion were observed when the crystal structure of the Eu$^{2+}$ doped SrAl$_2$O$_4$ material was optimized with the DFT calculations. The Eu-O distances were slightly shorter in the optimized structure compared to the original Sr-O distances, irrespective of Eu$^{2+}$ locating in the Sr1 or Sr2 site. This resulted in an increase in the electron repulsion shifting the Eu$^{2+}$ $4f^7$ ground state higher in the energy gap. Despite the small structural differences in the two Sr sites with structure optimization, a significant energy difference between the luminescence bands from SrAl$_2$O$_4$:Eu$^{2+}$ has been observed experimentally at low temperature. The difference may be explained rather by luminescence originating from a higher excited Eu$^{2+}$ $4f^65d^1$ state than in the $4f^7$ ground state position of Eu$^{2+}$ in the Sr1 and Sr2 site. The effect of the local environment – e.g. the presence of defects and defect aggregates – on the luminescence from the Eu$^{2+}$ center has yet to be studied in detail since it may have a significant contribution to the peculiar low temperature luminescence properties of SrAl$_2$O$_4$:Eu$^{2+}$.
Experimental Section

Electronic structure calculation. The electronic structure was calculated using the WIEN2k package\textsuperscript{13}. WIEN2k is based on the full potential linearized augmented plane wave method, an approach which is among the most precise and reliable ways to calculate the electronic structure of solids. In order to describe better the strongly correlated 4f electrons of Eu\textsuperscript{2+}, the GGA+U\textsuperscript{14} method was used. This method uses the semi-local spin density generalized gradient approximation (GGA), but for selected atomic states the DFT exchange-correlation potential is replaced by its Hartree-Fock-like form. To correct for the double counting the “Fully Localized Limit” version\textsuperscript{15} of the GGA+U method was used.

The GGA+U method requires as the input the Coulomb repulsion strength (Hubbard parameter $U$) and the exchange parameter $J$, which can be related to the Slater integrals\textsuperscript{16}. $U$ increases with increasing nuclear charge and valence state, whereas $J$ is almost independent of the number of nd (nf) electrons. Since both Gd\textsuperscript{3+} and Eu\textsuperscript{2+} have the rather similar 4f\textsuperscript{7} ground state configuration, the $U$ and $J$ values 7.62 and 0.68 eV, respectively, were used for the calculations concerning the Eu\textsuperscript{2+} ion since these parameter values have been found to reproduce the experimentally observed splitting between the majority and minority spin states of the Gd\textsuperscript{3+} ion\textsuperscript{17}. However, a somewhat smaller Hubbard parameter $U$ value for the Eu\textsuperscript{2+} ion is expected since the Gd\textsuperscript{3+} ion is much smaller than Eu\textsuperscript{2+} and thus the interelectronic repulsion in the much larger Eu\textsuperscript{2+} ion should be lower, too.

The reliable calculation of the electronic structure requires the optimization of the crystal structure of the Eu\textsuperscript{2+} doped materials. This was achieved by relaxing the atomic positions in the unit cell including one Eu\textsuperscript{2+} ion and three Sr\textsuperscript{2+} ions, while the external lattice parameters were not changed. The equilibrium position of each atom was calculated using the spin-polarized GGA method without the spin-orbit coupling. The optimized structure was then used to recalculate the electronic structure by employing the GGA+U method without the spin-orbit coupling.

Acknowledgements

Financial support is acknowledged from the Turku University Foundation, Jenny and Antti Wihuri Foundation (Finland) and the Academy of Finland (contract #117057/2006). The DFT calculations were carried out using the supercomputing resources of the CSC IT Center for Science (Espoo, Finland). The study was supported by research mobility agreements (112816/2006/JH and 116142/2006/JH, 123976/2007/TL) between the Academy of Finland and the Academy of Sciences of the Czech Republic as well as Czech research project AVOZ10100521 (PN).

Received: December 21, 2009.

Synchrotron Radiation Studies of Rare Earth Persistent Luminescence Materials

Jorma Hölsä¹,²,*, Aleksei Kotlov³, Taneli Laamanen¹,⁴ Mika Lastusaari¹,², Marja Malkamäki¹,⁴, Pavel Novák⁵

¹ University of Turku, Department of Chemistry, FI-20014 Turku, Finland
² Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland
³ Deutsches Elektronen-Synchrotron, Notkestrasse 85, D-22607 Hamburg, Germany
⁴ Graduate School of Materials Research (GSMR), Turku, Finland
⁵ Academy of Sciences of the Czech Republic, Institute of Physics, CZ-16253 Prague 6, Czech Republic
E-mail: jholsa@utu.fi, fax: +358-2-333 6730

Abstract. The electronic structure of the polycrystalline Sr₂MgSi₂O₇:Eu²⁺,R³⁺ (R³⁺: Ce³⁺, Dy³⁺, Yb³⁺) persistent luminescence materials was studied with the UV-VUV emission and excitation by synchrotron radiation. The band gap energy (Eg) was observed to increase with decreasing temperature in accordance with the Bose-Einstein model. The electronic defect structure of the Sr₂MgSi₂O₇:Eu²⁺,R³⁺ was investigated with thermoluminescence. Theoretical calculations using the Density Functional Theory (DFT) were carried out simultaneously with the experimental work to reveal the Eg value and the energy position of the different defects (i.e., Eu²⁺ substituting for Sr²⁺, oxygen -••O°- and strontium -••'M°- vacancies) in the host band structure. The experimental Eg value of 7.1 eV agrees well with the DFT value of 6.7 eV. All the defects studied (see above) induced density of state (DOS) close to the bottom of the conduction band. According to the mechanism of persistent luminescence from Sr₂MgSi₂O₇:Eu²⁺,R³⁺ presented, these DOS states can act as defect levels where the excitation energy can be stored and, eventually, liberated by thermal energy to be observed as persistent luminescence.

Keywords: Persistent luminescence; strontium disilicate; europium; synchrotron radiation; density functional theory; defects

Introduction

Persistent luminescence is a phenomenon where the material is emitting - usually in the visible range - for hours after the irradiation (or excitation) source has been switched off. Since the irradiation used may be in the form of practically any energy (γ-, X-, or UV radiation, visible light, IR radiation or thermal energy) persistent luminescence has not been looked at well at all in the conventional phosphor applications. Furthermore, owing to the admittedly complex mechanisms behind persistent luminescence and due to the general ignorance of these, persistent luminescence has been called with a litany of different names as afterglow, phosphorescence, long-lasting phosphorescence or any combination of them, in fact. Worst of all, persistent luminescence is still frequently, in a misleading manner, called phosphorescence because of the long emission time. Phosphorescence may be an appropriate term to be used in the context of luminescence from organic compounds involving triplet-to-singlet transitions. These are forbidden with a long decay time but are otherwise perfectly natural. According to the present knowledge, the long decay time of persistent luminescence, however, is due to the storage of the excitation energy in traps and its subsequent release from them with thermal energy. Thus the term thermally stimulated luminescence (TSL) is appropriate but for the sake of brevity, the phenomenon can be called as persistent luminescence.

The first persistent luminescence materials in commercial use were based on copper (and cobalt) doped zinc sulfides, ZnS:Cu,(Co)². Due to their short persistent luminescence and instability against moisture, their use was eventually rejected though not before causing serious delay in the development of more efficient persistent luminescence materials. The invention of the first persistent modern persistent luminescence materials, the alkaline earth


© 2010 NWT-Verlag, Bornheim, Germany
aluminates\textsuperscript{3} doped with Eu\textsuperscript{2+} and co-doped with selected rare earth (R\textsuperscript{3+}) ions as Dy\textsuperscript{3+} and Nd\textsuperscript{3+}, MA\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{2+}\textsuperscript{3},R\textsuperscript{3+} (M: Ca, Sr and Ba) initiated the systematic investigations of the thermally stimulated materials. Later the corresponding magnesium disilicates\textsuperscript{4}, M\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}:Eu\textsuperscript{2+},R\textsuperscript{3+}, have replaced the aluminates as the prime subject of scientific and commercial interest. Especially, the exact knowledge of the luminescence mechanisms and the trap identification has been targeted in these studies. Many a mechanism has been presented up to date with variable trustworthiness and innovation but, as a permanent result, several new research methods and new uses of ancient methods have been taken into use in these studies.

In this report, the use of the synchrotron radiation and thermoluminescence as a novel and as a novel use of a more conventional method, respectively, are presented in the study of persistent luminescence and the properties of the corresponding Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}:Eu\textsuperscript{2+},R\textsuperscript{3+} materials. It will be shown also that the Density Functional Theory (DFT) calculations can yield invaluable information about the defect structure in the persistent luminescence materials: the creation of energy levels in the band gap of the Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7} host by Eu\textsuperscript{2+} doping, R\textsuperscript{3+} co-doping, as well as by strontium and oxygen vacancies (V\textsubscript{Sr} and V\textsubscript{O}\textsuperscript{−}, respectively) may induce traps to accommodate energy to be used later for persistent emission.

Results and discussion

Emission of Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}:Eu\textsuperscript{2+},R\textsuperscript{3+}. The synchrotron radiation excited luminescence spectra of the M\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}:Eu\textsuperscript{2+} (M: Ca, Sr, Ba) materials (Fig. 1) are each composed of a strong band at ca. 550, 472, and 520 nm (18200, 21200 and 19200 cm\textsuperscript{-1}), respectively, due to the 4f\textsuperscript{5}d\textsuperscript{1} → 4f\textsuperscript{1} transition of the Eu\textsuperscript{2+} ion.\textsuperscript{5} The emission spectra are quite identical with those obtained with UV excitation\textsuperscript{4,6} though the excitation mechanisms are quite different. The energy transfer from the lattice to Eu\textsuperscript{2+} is thus very efficient. Despite the quite perfect match of the Ba\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}:Eu\textsuperscript{2+} emission to the sensitivity of the human eye, the emission of the strontium disilicate is the strongest of all three, also in the absolute scale. The Eu\textsuperscript{2+} ion is expected to occupy the M\textsuperscript{2+} sites in each M\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7} host though in the barium and calcium disilicates, there are local structural distortions to be expected due to the significant differences between the ionic radius of Eu\textsuperscript{2+} and Ba\textsuperscript{2+} as well as Ca\textsuperscript{2+}.\textsuperscript{10} In contrast, the size of Sr\textsuperscript{2+} is almost the same as that of Eu\textsuperscript{2+}. The local distortions are revealed in the widths of the emission bands: the FWHM value for the strontium disilicate (1730 cm\textsuperscript{-1}) is by far the smallest. For the monoclinic Ba\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7} host, it may also be possible that Eu\textsuperscript{2+} occupies more than one Ba\textsuperscript{2+} site though the latest structural data\textsuperscript{11} indicates only one Ba\textsuperscript{2+} site in the monoclinic Ba\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}.

Figure 1: Synchrotron radiation (SR) excited (time integrated) emission spectra of the M\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}:Eu\textsuperscript{2+} (M: Ca, Sr, Ba) materials at 10 K (SUPERLUMI, HASYLAB). The excitation takes place to the conduction band of the host (160 nm).

One should expect that the energy of the emission bands of Eu\(^{2+}\) in the Mg\(_2\)MgSi\(_2\)O\(_7\) hosts would evolve in line with the ionic radius of the Mg\(^{2+}\) host cation, most probably increasing with increasing ionic radius from calcium to barium disilicate. With band emission, this may be rather difficult to be observed but with the R\(^{3+}\) sharp line emission, as ROCl:Eu\(^{3+}\) (R: La, Gd, Y), this has been confirmed\(^{12}\). The experimental observation for the Mg\(_2\)MgSi\(_2\)O\(_7\) hosts is not supporting this simple conclusion. In fact, the energy of the Eu\(^{2+}\) emission, actually that of the lowest 4f\(^5\)5d\(^1\) level, is determined by two effects: the barycenter of the 4f\(^5\)5d\(^1\) configuration is expected to be at the highest energy in Ba\(_2\)MgSi\(_2\)O\(_7\) (lowest for Ca\(_2\)MgSi\(_2\)O\(_7\)) while the crystal field effect should then be the weakest (strongest for Ca\(_2\)MgSi\(_2\)O\(_7\)). The delicate interplay between these two effects results in an unorthodox behavior of the emission in the Mg\(_2\)MgSi\(_2\)O\(_7\) series.

The emission spectra of Mg\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\) reveals also the inherent problem of the use of Eu\(^{2+}\) emission as the source of persistent luminescence: the red emission is difficult to attain\(^{13}\). As usual, the calcium compound with the strongest crystal field and lowest 4f\(^5\)5d\(^1\) barycenter yields the lowest energy for the lowest 4f\(^5\)5d\(^1\) level but this is not enough for achieving red emission in the Mg\(_2\)MgSi\(_2\)O\(_7\) series. Despite the promising properties of the disilicate host, e.g. the high chemical stability and the evidently easy creation of defects in a way similar to mullite\(^{14}\), this host is not the one to solve the challenge of red persistent luminescence.

The persistent luminescence is well known to be enhanced by the R\(^{3+}\) co-doping in all the known Eu\(^{2+}\) doped persistent luminescence materials\(^{15}\). The same is true for the Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\) material, too (Fig. 2). What is less commonly recognized is that co-doping with every R\(^{3+}\) does not lead to the enhancement. In fact, some R\(^{3+}\) ions can seriously quench the persistent luminescence of Eu\(^{2+}\). The latter effect is the most common with the Sm\(^{3+}\) (and Yb\(^{3+}\)) co-doping and may be connected to the reduction of the trivalent ions to the divalent state followed by the destruction of Mg\(^{2+}\) vacancies\(^{16}\). However, the final explanation to this is still an open question. The quenching effect of Tm\(^{3+}\) co-doping in Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\) (Fig. 2) may support this explanation since Tm\(^{3+}\) may also be reduced to Tm\(^{2+}\) with relative ease.

![Figure 2: Time evolution of the UV excited persistent luminescence intensity of selected R\(^{3+}\) co-doped Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\) persistent luminescence materials at 295 K.](image)

The enhancement of persistent luminescence by the Nd\(^{3+}\) and Dy\(^{3+}\) co-doping in aluminates as CaAl\(_2\)O\(_4\)\(^{17}\) and SrAl\(_2\)O\(_4\)\(^{18}\), respectively, is a well-established fact. Similar enhancement by the use of these two co-dopants can be observed for Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\), too (Fig. 2). It should be noted, however, that the difference in the enhancing effect of these two ions is close to an order of magnitude. Taken into account the chemical similarity of the Nd\(^{3+}\) and Dy\(^{3+}\) ions, this difference is difficult to explain. One attempt to explain the persistent luminescence has been offered by the position of the R\(^{3+}\) energy levels close to the bottom of the conduction

\(^{13}\) J. Hölsä, ECS Interface 2009, 18(4), 42-45.
band of the Sr$_2$MgSi$_2$O$_7$ host$^{19}$. However, the difference between the Nd$^{3+}$ and Dy$^{3+}$ energy levels is such a trifle according to this diagram that some additional factors must be sought after.

The immediate effect of the R$^{3+}$ co-doping by the introduction of the R$^{3+}$ ions in the Sr$^{2+}$ site is the charge compensation. As a result of the reducing preparation conditions, the compensation of the excess positive charge of R$^{3+}$ cannot be carried out by the introduction of (interstitial) oxide but a creation of cation vacancy, most probably a Sr$^{2+}$ one, should rather be considered according to the following scheme:

$$3 \text{Sr}^{x^+} \rightarrow 2 \text{R}^{3+}_\text{Sr} + \text{V}^{2-}_\text{Sr} \tag{1}$$

In this scheme the Kröger-Vink notation$^{20}$ is followed and the species R$^{3+}_\text{Sr}$ represent a R$^{3+}$ ion in the Sr$^{2+}$ site with a positive net charge, V$^{2-}_\text{Sr}$ a strontium vacancy with a double negative charge and Sr$^{2+}_\text{Sr}$ a Sr$^{2+}$ ion in the Sr$^{2+}$ site with no net charge. The charges are counted as relative to the initial situation where double positive Sr$^{2+}$ ions are found. This charge compensation scheme is a somewhat more chemical explanation to the ability of the R$^{3+}$ ions to trap an electron which seem to be the charge carriers in the persistent luminescence from the Eu$^{2+}$ doped materials, at least$^{21}$. The electron traps are usually situated close to the bottom of the conduction band, at least when they can be the origin of the persistent luminescence since the electrons should be promoted from the traps with rather feeble thermal energy available at room temperature. At this point, the Eu$^{2+}$ emission from Sr$_2$MgSi$_2$O$_7$:Eu$^{2+},$R$^{3+}$ gives no further information about the persistent luminescence and other methods should be employed to investigate the trap structure in Sr$_2$MgSi$_2$O$_7$:Eu$^{2+},$R$^{3+}$.

**Trap Depths in Sr$_2$MgSi$_2$O$_7$:Eu$^{2+},$R$^{3+}$.** The thermoluminescence (TL) spectroscopy is the conventional method to study traps in solid state materials$^{22}$. Although this method is very sensitive, the identification of traps may prove to be rather challenging. Moreover, as for so many other thermoanalytical methods, the results depend somewhat on the experimental conditions as the heating rate, packing and amount of the sample as well as the irradiation time and energy, just to mention a few. It is thus evident that the exact reproduction of TL results, especially with a dissimilar experimental setup, is quite demanding. The TL glow curves of the Sr$_2$MgSi$_2$O$_7$:Eu$^{2+},$R$^{3+}$ materials are characterized by a strong band centered at ca. 80 to 90 °C as shown for the Sr$_2$MgSi$_2$O$_7$:Eu$^{2+},$Lu$^{3+}$ material (Fig. 3). This band can be considered as an intrinsic one common for the Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$ host irrespective of the R$^{3+}$ co-dopant.

![Figure 3: Analysis of the thermoluminescence glow curves of the Eu$^{2+}$ doped and Lu$^{3+}$ co-doped Sr$_2$MgSi$_2$O$_7$ with the deconvolution method according to the 2$^{nd}$ order kinetics model.](image)

The R$^{3+}$ co-doping modifies somewhat the glow curves, however, since there appear new or at least much stronger bands than without co-doping at higher temperatures, i.e. above 100 °C. Since these bands appear below

---


© 2010 NWT-Verlag, Bornheim, Germany
200 °C they are not really corresponding to deep traps similar to those present in photostimulated materials\textsuperscript{23}. The high temperature peaks should be regarded as extrinsic ones since their creation is due to the introduction of the R\textsuperscript{3+} co-dopant into the basic Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}:Eu\textsuperscript{2+} material.

Due to the nature of the TL emission corresponding to the emission of Eu\textsuperscript{2+} in Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}, one can try to deduce the origin of the TL bands. Evidently, the lattice defects as anion vacancies located very close to the bottom of the conduction band play the major role. The oxide vacancies, most likely due to the reducing preparation conditions, can trap electrons which are the source of the TL emission. Alternatively, the cationic defects created due to charge compensation when the R\textsuperscript{3+} ions replace for Sr\textsuperscript{2+} may act as hole traps, too. In addition to the simple isolated defect species, all kinds of aggregates of these electron traps with hole traps as strontium vacancies are probably present, as well\textsuperscript{24,25}.

As a result of the deconvolution procedure, a good agreement between the trap depths and the TL peak temperatures was obtained (Fig. 3). The width of the energy distribution of the traps is not very large, either, from virtually zero up to 0.5 eV\textsuperscript{26}. This would suggest only slight differences in the intensity and especially the duration of persistent luminescence obtained from materials with different co-dopants. However, since the persistent luminescence is controlled by the Boltzmann distribution, the actual experimental observations yield differences reaching up to several orders of magnitude in both aspects (Fig. 2).

### Trap Levels in Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}:Eu\textsuperscript{2+},R\textsuperscript{3+}

As pointed out above, the identification of the traps from the TL glow curves is difficult if not impossible. Since the trap levels should consist of the existing, though without irradiation of the material unoccupied levels in the band gap of the Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7} host, the density functional theory (DFT) calculations were carried out. The density of state (DOS) calculations were carried out in several consecutive steps: first, the electronic structure of the non-doped host was calculated. The results\textsuperscript{27} show that the experimental band gap energy of ca. 7.1 eV can be reproduced with good accuracy with the DFT calculation yielding the \(E_g\) value of ca. 6.7 eV. This is a definite improvement to calculations carried out on similar materials (Sr\textsubscript{2}Al\textsubscript{2}O\textsubscript{5}\textsuperscript{28} and Ca\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}\textsuperscript{29}) with discrepancies up to several eV. It should be noted concerning the present calculations that no density of state (i.e. possible trap levels) could be observed close to the bottom of the conduction band, in fact nowhere in the band gap (Fig. 4, the lowest curve).

![Figure 4: Calculated density of states of the non-doped, Eu\textsuperscript{2+} doped and Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7} with an isolated oxygen (and a strontium) vacancy located in the O1 (Sr) site (the GGA method used in the calculations).](image)

The next step of the calculations involved the calculation of the electronic structure of the Eu\textsuperscript{2+} doped Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}, i.e. with the aliovalent Eu\textsubscript{Sr}\textsuperscript{2+} defect where the Kröger – Vink notation \(\times\) means a defect with no net charge (when compared to the initial non-doped system). Since the Eu\textsuperscript{2+} and Sr\textsuperscript{2+} ions are of the same size\textsuperscript{30}, one should not expect any changes in the electronic structure of the Sr\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7} when compared to the non-doped host. Some important differences due to Eu\textsuperscript{2+} doping are obtained, however. First of all, the \(4f^{6–1}5d^1\) levels which


© 2010 NWT-Verlag, Bornheim, Germany
should not be too easily (i.e. not reliably) obtained by the DFT calculations were observed just below the bottom of the conduction band forming a quasi continuous DOS (Fig. 4, 2\textsuperscript{nd} curve from the bottom). This is a theoretical verification of the empirical position of the \( R^{2+} 4f^{n-1}5d^n \) levels close to the conduction band\textsuperscript{19}. This position of the \( 4f^{n-1}5d^n \) levels also gives support to the mechanism of (cf. next section) persistent luminescence which requests the easy removal of the excited electrons from the \( 4f^{n-1}5d^n \) levels into the conduction band.

As a second result, the energy level position of the \( \text{Eu}^{3+} \) ground level was found in the band gap of the host and is in a fairly good agreement with the predictions made using the empirical model of the \( R^{2+} \) energy level positions\textsuperscript{19}. Finally, to some surprise, there was found some discrete DOS close to the bottom of the conduction band. Although the depth of these levels below the conduction band is just a little bit too much when compared to the trap depths obtained from the thermoluminescence studies\textsuperscript{26}, they can be taken as the intrinsic trap levels of the \( \text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+} \) material. The results are very encouraging though no exact match with the experimental results was obtained. This could, however, be anticipated since in the actual materials there are more defects and aggregates of them to complicate things with mutual interactions.

The DFT calculations were thus continued with the inclusion of different defects. First, the strontium vacancies (\( V_{Sr} \)) were introduced to the “virtual” \( \text{Sr}_2\text{MgSi}_2\text{O}_7 \) material since these defects should be created by the \( R^{3+} \) co-doping. In a way, though not in an entirely comprehensive way, this simulates the effect of \( R^{3+} \) co-doping. The \( V_{M} \) defect was introduced as an isolated one since the charge compensation was assumed to be far away thus allowing the uncomplicated treatment of this defect without mutual interactions between the defect and its charge compensation. At the end, however, these interactions should be accounted for. Once again, one should not anticipate any changes around the bottom of the conduction band.

To start with the probability of this kind of defect, the creation of the \( V_{Sr} \) defect requires a substantial amount of energy since the total energy of the system is increased from \(-417\) to \(-331\) keV. As a result of the \( V_{M} \) defect, the band gap energy is increased by ca. 0.4 eV (Fig. 4, 3\textsuperscript{rd} curve from the bottom). This may be explained by a decrease in the DOS since the bottom of the conduction band\textsuperscript{27} has the predominantly strontium character. The actual \( V_{Sr} \) states are located very close to the top of the valence band corresponding to shallow hole traps in the material. Since these states are almost continuous with the valence band states, no actual hole trapping can be expected, at least not at room temperature. Eventually, a discrete \( V_{Sr} \) state is located at ca. 1 eV below the bottom of the conduction band. This level can possibly act as a rather shallow electron trap. Together with \( \text{Eu}^{2+} \), this may indicate a creation of several electron traps as was found in the \( \text{Eu}^{2+} \) doped \( \text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+} \) from the analysis of the TL glow curves (Fig. 3.).

The final step in the present DFT calculations, the introduction of the oxygen vacancy (\( V_{O}^{\cdot\cdot\cdot} \)) defect, was found to occur with only a small increase in the total energy of the system from \(-417\) to \(-415\) keV. This may be an indication that the reducing preparation conditions can indeed create such a defect. As for the electronic structure of \( \text{Sr}_2\text{MgSi}_2\text{O}_7 \), discrete oxygen vacancy state is located at 1.4 eV above the top of the valence band indicating the presence of a deep electron trap. However, electrons in the deep traps as this one are not available for the persistent luminescence due to the high amount of energy required to bleach the traps. In addition to this discrete trap level, several \( V_{O}^{\cdot\cdot\cdot} \) states are located close to the bottom of the conduction band, as well. These states indicate the presence of shallow electron traps which are readily bleached by the thermal energy at room temperature. These trap levels are too shallow and cannot be observed with the present TL measurements since they require lower that room temperatures.

As a result of the DFT calculations, a wealth of novel information was obtained about the probabilities of creating different defects in the \( \text{Sr}_2\text{MgSi}_2\text{O}_7 \) host lattice and about the modification of the electronic structure of this host by the defects. It should, however, be noted that the interactions between the different defects will definitely affect the exact energy levels of the defects. This is more important than generally anticipated since the persistent luminescence depends on the thermal excitation of electrons from the traps and thus even very minute differences in the trap depths can have a drastic influence to the performance of the persistent luminescence materials.

**Persistent Luminescence Mechanism.** The final aim of the work carried out above was to assess the credibility of the different persistent luminescence mechanisms presented in the literature. Since 1995, there have been a wealth of reports published on persistent luminescence of different \( \text{Eu}^{2+} \) based materials, including \( \text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+} \), but only a few mechanisms have outlived to date. One of the most logical mechanisms with a minimum of contradictions and confusion can be applied to the \( \text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+} \) materials as follows (Fig. 5): the irradiation of the material by blue light (or UV radiation) involves the photoexcitation of \( \text{Eu}^{2+} \) via the \( 4f^{n}5d^{1} \) levels which, as stated above, overlap with the conduction band of \( \text{Sr}_2\text{MgSi}_2\text{O}_7 \). The removal of the electrons can be either direct or assisted by thermal energy, depending on the energy difference between the \( 4f^{n}5d^{1} \) levels and the conduction band. The capture of the excited electron to the conduction band together with its free movement therein, leads to the eventual capture of the electrons by traps close to the bottom of the conduction band. Of course, not all the electrons are trapped but they can be returned to the europium centre, too.
The efficiency of persistent luminescence is, however, the higher the more general the capture is. It should be noted that despite the photoionization of Eu\(^{2+}\) the presence of trivalent Eu\(^{3+}\) has never been proven unambiguously, instead, the creation of a Eu\(^{2+}\)-h\(^+\) pair may be a more refined choice.

Figure 5: Persistent luminescence mechanism for the Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\)(,Lu\(^{3+}\)) materials.

The actual persistent luminescence involves the temperature controlled gradual release of the trapped electrons followed by the migration of electrons to Eu\(^{2+}\) through the conduction band for the recombination. No evident pitfalls exist in this mechanism though proving this is hard due to the ubiquitous uncertainty about the thermally controlled mechanism.

Conclusions

The combined use of thermoluminescence (TL) and UV-VUV spectroscopy as well as density functional theory (DFT) calculations was employed to reveal the defect levels of the Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\) persistent luminescence materials. The experimental band gap value of Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\) could be calculated with the density functional theory with a very good agreement. The 4f\(^7\) ground level position of Eu\(^{2+}\) fits well in the band gap of Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\). It should be recognized, however, that in order to predict in a reliable manner the energy level positions of the dopants and co-dopants, Eu\(^{2+}\) and R\(^{3+}\), their mutual interactions should be accounted for in the DFT calculations.

Experimental Section

Materials Preparation. The polycrystalline Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\) (R\(^{3+}\): none, Lu\(^{3+}\)) materials were prepared with a solid state reaction between stoichiometric amounts of SrCO\(_3\), Mg(NO\(_3\))\(_2\)**6H\(_2\)O, SiO\(_2\) and R\(_2\)O\(_3\) (R\(^{3+}\): Eu\(^{3+}\); Lu\(^{3+}\)). The nominal concentration of both Eu\(^{2+}\) and Lu\(^{3+}\) was one mole per cent of the strontium amount. The starting materials were ground to a homogeneous mixture in a ball mill. The mixtures were then annealed in a reducing (N\(_2\)+ 10 % H\(_2\)) atmosphere first for one and then for ten hours at 700 and 1350 °C, respectively. The structural and phase purity was confirmed by X-ray powder diffraction using a Huber G670 image plate Guinier-camera at 295 K (CuK\(_{\alpha}\) radiation, 1.5406 Å). No additional phases were found in the materials.

Synchrotron Radiation Measurements. The UV-VUV excitation spectra of the Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\) (R\(^{3+}\): none, La\(^{3+}\)) materials were measured between 3.7 and 40 eV by using the synchrotron radiation at the SUPERLUMI beam line of HASYLAB at DESY (Hamburg, Germany). The samples were mounted on the cold finger of a liquid He flow cryostat. The spectra were recorded at selected temperatures between 10 and 298 K with a 2-m McPherson type primary monochromator attaining a resolution up to 0.02 nm. The emission spectra were obtained with a Spectra Pro 300i monochromator (200 to 800 nm) equipped with a conventional photomultiplier and/or with a CCD detector (200 to 1050 nm).

Thermoluminescence Measurements. The thermoluminescence (TL) glow curves of the Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\),R\(^{3+}\) (R\(^{3+}\): none, La\(^{3+}\)) materials were recorded with a Risø TL/OSL-DA-12 apparatus with a heating rate of 5 °Cs\(^{-1}\).
About 40-80 mg samples of the materials were used for these experiments. Prior to the TL measurements, the materials were exposed to radiation from a combination of two UV lamps: Philips TL 20W/05 (maximum emission at 380 nm) and TL 20W/03 (420 nm).

**Density Functional Theory Calculations.** The electronic structures of defect free, Eu$^{2+}$ doped, oxygen or strontium vacancy containing Sr$_2$MgSi$_2$O$_7$ were calculated using the WIEN2k package$^{30}$. WIEN2k is based on the full potential linearized augmented plane wave method, an approach which is among the most precise and reliable ways to calculate the electronic structure of solids. The Generalized Gradient Approximation (GGA) method was employed. The reliable calculation of the electronic structure requires the optimization of the crystal structure with a defect, either a strontium or oxygen vacancy or Eu$^{2+}$ substituting for Sr$^{2+}$. This was achieved by relaxing the atomic positions in the unit cell, while the lattice parameters were not changed. The equilibrium position of each atom was calculated using the GGA method. The strontium or oxygen vacancy was treated here as an isolated defect since no charge compensation was included in the unit cell. The vacancy aggregation (e.g. adjacent $V_s^o$ and $V_o^o$) as well as the modification of the defect electronic structure due to the neighboring Eu$^{2+}$/R$^{3+}$ ions were not considered in the calculations but is one of the subjects of further studies.

**Acknowledgements.**

Financial support is acknowledged from the Turku University Foundation, Jenny and Antti Wihuri Foundation (Finland) and the Academy of Finland (contract #117057/2006). The DFT calculations were carried out using the supercomputing resources of the CSC IT Center for Science (Espoo, Finland). The study was supported by research mobility agreements (112816/2006/JH and 116142/2006/JH, 123976/2007/TL) between the Academy of Finland and the Academy of Sciences of the Czech Republic. The synchrotron radiation study (HASYLAB, Germany) was supported by the European Community-Research Infrastructure Action under the FP6 Structuring the European Research Area Programme, RII3-CT-2004-506008 (IA-SFS). Prof. Kari O. Eskola and Prof. Högne Jungner (University of Helsinki, Helsinki, Finland) are acknowledged for the thermoluminescence measurements.

---


© 2010 NWT-Verlag, Bornheim, Germany
Effect of Grinding on the UV Excited and Persistent Luminescence of SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$

Jorma Hölsä$^{1,2}$, Högne Jungner$^3$, Mika Lastusaari$^{1,2}$, Marja Malkamäki$^{1,4,*}$ and Janne Niittykoski$^1$

$^1$ University of Turku, Department of Chemistry, FI-20014 Turku, Finland
$^2$ Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland
$^3$ University of Helsinki, Dating Laboratory, FI-00014 Helsinki, Finland
$^4$ Graduate School of Materials Research (GSMR), Turku, Finland
E-mail: marja.malkamaki@utu.fi

Abstract. The SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ ($x_{Eu}$: 0.01 and $x_{Dy}$: 0.02) material prepared with a solid state reaction was ground for one to ten minutes. A commercial product (Luminova, United Mineral & Chemical Corp.) was ground for 10 minutes, as well. According to the X-ray powder diffraction measurements, both the fresh and commercial materials consist of the monoclinic SrAl$_2$O$_4$. Grinding does not cause significant changes in the shape and width of the reflections. The UV excited ($\lambda_{exc}$: 350 nm) and persistent emission consists of a broad band at 520 nm due to the 4f$^6$5d$^1$$\rightarrow$4f$^7$ emission of Eu$^{2+}$. Grinding weakens both the UV excited and persistent luminescence of both the fresh and commercial materials. Thermoluminescence (TL) glow curves of the fresh materials have a band at ca. 90 °C which corresponds to shallow traps. Above this temperature, a broad band at ca. 130-300 °C embraces several individual bands corresponding to deep traps. The TL glow curves of the commercial product consist of a very strong and broad band in the range of 40 to 250 °C. The grinding reduces drastically the high temperature TL bands of the fresh material but has only a slight effect to the TL properties of the commercial material. The different behavior of the two materials indicates differences in the co-dopants and/or their concentrations as well as in the preparation conditions of the materials.

Keywords: Strontium aluminate; Eu$^{2+}$; Persistent luminescence; Grinding

Introduction

Persistent luminescence is a phenomenon where the material continues to emit in visible far after the irradiation source has been removed. The conventional persistent luminescence material is ZnS:Cu which is, however, very sensitive to moisture and, moreover, the duration of persistent luminescence is only a few hours$^1$. As a consequence of its mediocre performance, nowadays it is replaced by Eu$^{2+}$ and rare earth doped aluminates$^2$ (e.g. SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$) and disilicates$^3$ (e.g. Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$,Dy$^{3+}$). These materials are more stable and their persistent time is longer – they can emit light for up to 15-25 hours.

In general, the Eu$^{2+}$ doped solid state materials emit strong broad band luminescence with a short decay time$^1$, around one µs. When Eu$^{2+}$ is doped into strontium aluminate (SrAl$_2$O$_4$:Eu$^{2+}$), the emission can be observed for several hours after ceasing of irradiation$^4$. The duration and intensity of persistent luminescence from SrAl$_2$O$_4$:Eu$^{2+}$ can be improved drastically by adding selected trivalent rare earth ions as co-dopants$^5,6,7$. Especially the Dy$^{3+}$ co-doping enhances the persistent luminescence$^2$. This effect is probably due to an increase

in the number and/or density of traps and modification of their depths by the co-dopants. The mechanism of persistent luminescence is not known in detail but it is frequently related to the trapping of electrons and/or holes leading to the storage of energy. The electrons/holes are eventually thermally released from traps and the release is followed by the Eu$^{3+}$ emission$^8$.

It is commonly assumed that grinding of persistent luminescence materials deteriorates the luminescence intensity. Indeed, earlier studies of the effect of grinding$^{10,13}$ have revealed that the grinding lowers the intensity of UV excited luminescence. This effect is often explained by an enhancement of nonradiative transitions and scattering of both the exciting and emitted radiation. It may also be a consequence of the creation of new traps or the decomposition of luminescent centres. There might be a simultaneous influence of some of these factors, too. Nevertheless, the effect of grinding on persistent luminescence has not been studied previously.

The aim of this work was to study the effect of grinding to the luminescence properties of SrAl$_2$O$_4$:Eu$^{3+}$:Dy$^{3+}$ and to carry out a comparison to a corresponding commercial material. A fresh SrAl$_2$O$_4$:Eu$^{3+}$:Dy$^{3+}$ material was prepared with a solid state reaction and ground in an agate mortar for different periods of time: 1, 4, 7 and 10 minutes. Materials’ structure and purity was studied with X-ray powder diffraction (XPD). The emission spectra of UV excited and persistent luminescence were measured at room temperature whereas the thermoluminescence (TL) glow curves were measured between 0 and 400 °C. The XPD, luminescence and TL measurements were also carried out with a corresponding commercial material (Luminova, United Mineral & Chemical Corp.).

**Results and discussion**

**Crystal structure and purity.** The fresh and commercial samples consist (Fig. 1) predominantly of the monoclinic SrAl$_2$O$_4$ phase (space group P2$_1$, No. 10; Z: 4) with a, b, c, and $\beta$ equal to 8.447, 8.816, 5.163 Å and 93.4°, respectively$^{14}$. In addition to the desired SrAl$_2$O$_4$ phase, a small amount of SrAl$_5$O$_{12}$ was observed as an impurity phase in both samples. In the commercial product, some unknown impurities were observed, too. The latter impurities possibly originate from other compounds used in the preparation process or from additional co-dopants.

Grinding does not cause significant changes in the shape and width of the XPD reflections. This means that the crystallite size remains unchanged despite the grinding. Some of the impurity reflections weaken with increasing grinding time but, at the same time, some of them get stronger. Because of this, it is possible that the impurities in the commercial material can originate from two or more compounds.

![Figure 1. Effect of grinding on the XPD patterns of a fresh (left) and commercial (right) SrAl$_2$O$_4$:Eu$^{3+}$:Dy$^{3+}$ material (**: SrAl$_2$O$_4$; *: unknown). The reference pattern was calculated with the PowderCell program$^{16}$ using the crystallographic data from$^{14}$.](image)

---

15 JCPDS, 1997, POWDER DIFFRACTION FILE, entry 10-0065 (SrAl$_2$O$_4$).

© 2010 NWT-Verlag, Bornheim, Germany
UV excited and persistent luminescence. The green emission of $\text{SrAl}_2\text{O}_4\text{Eu}^{2+},\text{Dy}^{3+}$ consists of a broad band centred at 520 nm due to the $4f^85d^1(\text{^2}D) \rightarrow 4f^9(\text{^8}S_{7/2})$ transition of $\text{Eu}^{2+}$ (Fig. 2). In general, the luminescence of $\text{SrAl}_2\text{O}_4\text{Eu}^{2+},\text{Dy}^{3+}$ weakens with increasing grinding time though there exists problems in the reproducibility of quantitative intensity measurements. The weakening of luminescence is an indication that the grinding introduces traps strongly quenching the luminescence. This is clear though differences are small and measurements are susceptible to random errors. The luminescence of the commercial material is stronger than that of the fresh material which is possibly due to the larger crystal size and different $\text{Eu}^{2+}$ concentration. After grinding the commercial material for ten minutes, the luminescence is as weak as the luminescence from the corresponding fresh material which indicates that the commercial material suffers drastically from grinding and the advantage of its better initial luminescence properties is lost.

The persistent luminescence of $\text{SrAl}_2\text{O}_4\text{Eu}^{2+},\text{Dy}^{3+}$ has also the maximum at 520 nm and it is due to the same $4f^85d^1 \rightarrow 4f^9$ transition of the $\text{Eu}^{2+}$ ion as in the UV excited luminescence (Fig. 2). The persistent luminescence from both materials weakens with increasing grinding time though the persistent luminescence of the commercial product is much stronger. The difference in the persistent luminescence intensity may be due to the different concentrations of the $\text{Eu}^{2+}$ and $\text{Dy}^{3+}$ ions when compared to the fresh material. There is also some indication that there might be additional co-dopants in the commercial material which enhance the persistent luminescence. For example, it has been reported that the brightness and duration of the persistent luminescence from $\text{SrAl}_2\text{O}_4\text{Eu}^{2+},\text{Dy}^{3+}$ may be improved with Tb$^{3+}$ or Yb$^{3+}$ co-doping.$^{17,18}$ The different luminescence properties of the commercial product might also be due to the different preparation method or conditions which are not known in detail. The preparation of the aluminates with the use of borate flux is rather complicated and allows countless possibilities to modifications.

Thermoluminescence. The thermoluminescence (TL) glow curves of the fresh $\text{SrAl}_2\text{O}_4\text{Eu}^{2+},\text{Dy}^{3+}$ materials have a band at ca. 90 °C which corresponds to quite shallow traps (Fig. 3). Above this temperature, a broader band at ca. 130-300 °C probably embraces several individual bands corresponding to deeper traps. Grinding affects mostly the deep traps by essentially removing them. This weakens the energy storage properties of the material and, consequently, the persistent luminescence is weakened. For the sample ground for seven minutes, the band corresponding to shallow traps is moved to 80 °C, as well. Generally, the heat conduction of a material becomes faster due to grinding and thus the TL bands will be observed at lower temperatures. However, this is not observed for the sample ground for ten minutes. When the TL curves of the fresh materials are deconvoluted four traps are revealed (Fig. 4). The trap depths range from 0.6 to 1.0 eV and all of the bands follow the 2$^\text{nd}$ order kinetics indicating retrapping.

The TL glow curves of the commercial $\text{SrAl}_2\text{O}_4\text{Eu}^{2+},\text{Dy}^{3+}$ material consist of a very strong and broad band in the range of 40 to 250 °C (Fig. 3) which evidently corresponds to several traps. The deconvoluted TL curves

---

reveal at least three traps (Fig. 4) with trap depths ranging from 0.6 to 1.1 eV. The grinding of the commercial material weakens somewhat the total TL intensity which leads to weaker persistent luminescence, too. The trap energy range and the energies of individual traps are, however, essentially the same for the both materials. The only difference is the absence (or weakness) of the deepest trap for the commercial material. This may partially explain the superior performance of the commercial material since the loss of energy stored in the deep traps is avoided. It is thus evident that the additional co-dopants and/or modifications in preparation have managed to stabilize the trap structure of the commercial material.

Figure 3. Effect of grinding on the TL glow curves of the fresh (left) and commercial (right) SrAl\(_2\)O\(_4\):Eu\(^{2+}\),Dy\(^{3+}\) materials.

Figure 4. Deconvoluted TL curve of the fresh (left) and commercial (right) SrAl\(_2\)O\(_4\):Eu\(^{2+}\),Dy\(^{3+}\) materials.

Conclusions

Both the fresh and commercial SrAl\(_2\)O\(_4\):Eu\(^{2+}\),Dy\(^{3+}\) materials consist of the same monoclinic SrAl\(_2\)O\(_4\) phase. The compound impurities are essentially the same confirming the quite similar preparation method/conditions though there are slightly more impurities in the commercial material. The UV excited and persistent luminescence spectra of the two SrAl\(_2\)O\(_4\):Eu\(^{2+}\),Dy\(^{3+}\) materials both comprise a broad band peaking at 520 nm which is due to the 4f\(^6\)5d\(^1\)(4D) \(\rightarrow\) 4f\(^7\)(6S\(_{7/2}\)) transition of Eu\(^{2+}\). Grinding does not change the crystallite size though it weakens both the UV excited and persistent luminescence from both materials. The persistent luminescence from the commercial material is much stronger than from the fresh material suggesting the use of additional co-dopants. The TL glow curves of both materials show shallow and deep traps and the deconvolution of the TL curves reveals the presence of up to four traps. The grinding mostly removes the deep traps leading to weaker energy storage in the fresh material. The TL intensity of the commercial material weakens only slightly due to grinding which indicates that the additional co-dopants have managed to stabilize the trap structure.
Experimental Section

Materials preparation. The polycrystalline SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ material was prepared with a solid state reaction between strontium carbonate (SrCO$_3$), aluminium oxide (Al$_2$O$_3$), europium oxide (Eu$_2$O$_3$) and dysprosium oxide (Dy$_2$O$_3$). The nominal concentrations of the Eu$^{2+}$ and Dy$^{3+}$ ions were 1 and 2 mole per cent of the strontium amount, respectively. 1 mole per cent of boron oxide (B$_2$O$_3$) was added to the mixture as a flux. The starting materials were ground to a homogenous mixture using a ball mill. The mixture was annealed in a reducing N$_2$ + 10% H$_2$ atmosphere at 900 °C for 1 h and at 1300 °C for 4 h. The commercial SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ material Luminova (United Mineral & Chemical Corp.) was studied as well. The preparation method and conditions as well as the Eu$^{2+}$ and Dy$^{3+}$ concentrations for this material are not known in detail.

The fresh SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ material was divided into four samples. Every sample was ground in an agate mortar for different periods of times (1, 4, 7 and 10 minutes). The commercial samples without and with grinding (10 minutes) were studied as well. The structural and phase purity of the samples was confirmed with X-ray powder diffraction using a Huber G670 image plate (2θ range: 4-100°) Guinier camera at 298 K (CuK$_\alpha$ radiation, 1.5406 Å). Measured patterns were compared to the calculated ones obtained using the program PowderCell.

UV excited and persistent luminescence measurements. The UV excited and persistent luminescence spectra at 295 K were measured with a Perkin-Elmer LS-5 spectrometer using a 15 W Xe lamp as the excitation source. Prior to the persistent luminescence measurements, the materials were irradiated with a 11 W tricolor fluorescent lamp. All luminescence measurements were repeated five times and presented as an average.

Thermoluminescence measurements. The TL glow curves were measured with a Risø TL/OSL-DA-12 system using a heating rate of 5 °Cs$^{-1}$ in the temperature range of 0 to 400 °C. The global TL emission from UV to 650 nm was monitored. Prior to the TL measurements, the samples were irradiated by a combination of the Phillips TL 20W/05 (emission maximum at 360 nm) and TL 20W/03 (420 nm) UV lamps for 60 to 120 s. A delay time of 3 min between the irradiation and measurement was used. The analysis of the TL glow curves was carried out by deconvoluting the TL curves with the program TLanal v.1.0.3$^{19,20}$ which uses the general approximation (GA) method as a background. The fitted peaks were considered to be of the 2$^{nd}$ order kinetics because of the symmetrical peak shape.

Acknowledgements

Financial support from the Academy of Finland (project #8117057/2006) to M.M. is acknowledged. Dr. Kari O. Eskola (Dating Laboratory, University of Helsinki, Helsinki, Finland) is acknowledged for the help with the TL measurements.

Received: December 23, 2009.

$^{19}$ K.S. Chung, TL Glow Curve Analyzer v.1.0.3., Korea Atomic Energy Research Institute and Gyeongsang National University in Korea, 2008.

Preparation and Up-Conversion Luminescence Properties of NaYF$_4$:Yb$^{3+}$,Er$^{3+}$ Nanomaterials

Iko Hyppänen$^{a,b}$, Jorma Hölösa$^{a,c}$, Jouko Kankare$^{a,c}$, Mika Lastusaari$^{a,c}$, Laura Pihlgren$^{a,d,*}$, and Tero Soukka$^e$

$^a$University of Turku, Department of Chemistry, FI-20014 Turku, Finland
$^b$Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM), Espoo, Finland
$^c$Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland
$^d$Graduate School of Materials Research (GSMR), Turku, Finland
$^e$University of Turku, Department of Biotechnology, FI-20520 Turku, Finland
E-mail: laura.pihlgren@utu.fi, fax: +358-2-333 6700

Abstract. The NaYF$_4$ host materials are among the most feasible lattices for efficient up-conversion. In this work, up-converting NaYF$_4$:Yb$^{3+}$,Er$^{3+}$ nanomaterials were obtained with the co-precipitation synthesis. The purity of the materials was investigated with FT-IR spectroscopy. The thermal behavior of the as-prepared materials was studied with thermogravimetry and differential thermal analysis. The crystal structure and phase purity were studied with X-ray powder diffraction and the crystallite sizes were calculated with the Scherrer formula from the diffraction data. The up-conversion luminescence was studied with NIR laser excitation at 970 nm. The FT-IR spectra showed that there were no organic impurities in the NaYF$_4$:Yb$^{3+}$,Er$^{3+}$ nanomaterials.

The thermal analysis revealed both exothermic and endothermic reactions due to the phase transitions of the material. The X-ray powder diffraction measurements revealed that there was present both the efficiently up-converting hexagonal and comparably poorer cubic phase depending, among other things, on the heating temperature and the gas sphere. The crystallite size was approximately 60-150 nm. The up-conversion luminescence spectra showed both strong red (640-685 nm) and green (515-560 nm) emission due to the $^{4}I_{15/2}$→$^{4}I_{11/2}$, $^{2}H_{11/2}$, $^{4}S_{3/2}$→$^{4}I_{15/2}$ transitions of Er$^{3+}$, respectively. The most intense up-conversion luminescence was obtained when the material was heated at 700 °C for 5 hours in the N$_2$ gas sphere.

Keywords: Up-Conversion Luminescence; NaYF$_4$:Yb,Er; Nanomaterials; Co-precipitation synthesis

Introduction

The phosphors transforming two or more low energy (IR) photons to visible light$^{1,2}$ have many potential applications in optoelectronic devices as lasers and displays as well as in inks for security printing (e.g. bank notes, bonds)$^{3-5}$. As a novel field of application, nanomaterials with efficient up-conversion luminescence may be used in the homogeneous label technology for quantitative all-in-one whole blood immunoassay$^{6-8}$.

The NaYF$_4$ host lattice has two crystal structures: cubic $\alpha$-NaYF$_4$ and hexagonal $\beta$-NaYF$_4$$^{9,10}$. In the cubic structure, the cation sites are equal and the Na and Y atoms are distributed randomly in the cation sublattice.
while in the hexagonal structure, there are three different types of cation sites\textsuperscript{12-14}. The highest up-conversion luminescence efficiency has been observed from the hexagonal, Yb\textsuperscript{3+} and Er\textsuperscript{3+} co-doped NaYF\textsubscript{4} material due to the very low phonon energy of the NaYF\textsubscript{4} lattice\textsuperscript{15}. Although some chloride and bromide lattices show enhanced up-conversion luminescence, most of them are sensitive to moisture\textsuperscript{16}. They might not be suitable for labeling biomolecules which are used mostly in aqueous solutions.

In this work, up-converting NaYF\textsubscript{4}:Yb\textsuperscript{3+},Er\textsuperscript{3+} nanomaterials were obtained with the co-precipitation synthesis\textsuperscript{17}. Also the role of EDTA in the formation of the size-controlled, monodispersed NaYF\textsubscript{4}:Yb\textsuperscript{3+},Er\textsuperscript{3+} nanoparticles was studied. EDTA is a strong chelating agent for rare earth (R) ions and forms stable R-EDTA complexes. EDTA has been claimed to prevent the particle aggregation by shielding the rare earth ions which is a necessity for the preparation of monodispersed particles\textsuperscript{18}. As for the size effect, chelation of the metal ions with EDTA should decrease the rate of both the nucleation process and the nucleus growth, resulting in a smaller particle size.

The purity of the NaYF\textsubscript{4}:Yb\textsuperscript{3+},Er\textsuperscript{3+} nanomaterials was analyzed with FT-IR spectroscopy. The preparation of the materials was studied with thermal analysis. The crystal structure was studied with X-ray powder diffraction. The crystallite sizes were also estimated with the Scherrer formula\textsuperscript{19} from the diffraction data. Up-conversion luminescence was studied with NIR laser excitation at 970 nm.

### Materials purity

The FT-IR spectra (Fig. 1) revealed that in the materials, with both the cubic and hexagonal phases, there are metal-fluoride vibrations of both phases; at 550 and ca. 400 cm\textsuperscript{-1} for the cubic and hexagonal phase, respectively. The strong HOH bending and OH stretching vibrations at 1550 and 3350 cm\textsuperscript{-1}, respectively, were mainly due to the water absorbed on the surface of the KBr discs during their preparation.

![Figure 1. FT-IR spectra of the NaYF\textsubscript{4}:Yb\textsuperscript{3+},Er\textsuperscript{3+} nanomaterials prepared with EDTA and annealed at selected temperatures.](image)

### Thermal behavior

The DTA curve of the NaYF\textsubscript{4}:Yb\textsuperscript{3+},Er\textsuperscript{3+} nanomaterial prepared with EDTA showed an exothermic reaction at 500 °C due to the formation of the hexagonal phase from the cubic one present at lower temperatures (Fig. 2). An endothermic reaction at 665 °C due to the formation of high temperature cubic phase from the hexagonal one was observed, too. The DTA curve of the NaYF\textsubscript{4}:Yb\textsuperscript{3+},Er\textsuperscript{3+} nanomaterial prepared without EDTA (Fig. 2) showed an exothermic reaction at 440 °C and an endothermic one at 660 °C due to the phase transitions described above. This revealed that the preparation of the nanomaterial with EDTA needs higher temperature for the formation of the hexagonal phase. This might be due to the EDTA preventing the particle growth. The crystallite size of the hexagonal phase seems in most cases to be larger than that of the cubic ones and because of

that, higher temperatures are needed for the cubic phase to change to the hexagonal one. The EDTA had practically no effect on the hexagonal to high-temperature cubic phase transition temperature.

![Figure 2. TG and DTA curves of the NaYF₄:Yb³⁺,Er³⁺ nanomaterial prepared with (left) and without EDTA (right).](image)

**Crystal structure and phase purity**

The crystal structure of the NaYF₄:Yb³⁺,Er³⁺ nanomaterials prepared with EDTA was cubic (Fm$\overline{3}$m (#225), Z: 2) below the annealing temperature of 400 °C, a mixture of cubic and hexagonal (P6$_3$ (#174), Z: 1.5) between 400 and 600 °C and cubic again above 700 °C (Fig. 3) when annealed in a N₂ + 10 % H₂ gas sphere. The structure of the as-prepared NaYF₄:Yb³⁺,Er³⁺ material was cubic.

![Figure 3. X-ray powder diffraction patterns of the NaYF₄:Yb³⁺,Er³⁺ nanomaterials annealed at selected temperatures (prepared with EDTA, left) and gas spheres (prepared without EDTA, right).](image)

The annealing in a N₂ + 10 % H₂ gas sphere at 600 °C produced only the hexagonal phase whereas a small amount of the cubic phase was present in the materials annealed in air or in N₂ when prepared without EDTA (Fig. 3). There was more cubic phase present in the material prepared with EDTA. This is in agreement with the suggestion presented above that the use of EDTA thwarts the formation of the hexagonal phase. There was also a small amount of the C₃R₂O₇ impurity in the material prepared without EDTA and annealed for 5 h at 600 °C in N₂ + 10 % H₂. The calculated crystallite sizes were ca. 60-150 nm for the cubic phase and ca. 150 nm for the hexagonal one.

---

20 PCPDFWIN v. 1.30, Powder diffraction file, International Centre for Diffraction Data, entries 06-0342 (cubic NaYF₄) and 28-1192 (hexagonal Na(Y$_{0.57}$Yb$_{0.39}$Er$_{0.04}$)F₄).
Up-conversion luminescence

The up-conversion luminescence was excited by NIR radiation (λexc: 970 nm). The excitation process for the up-conversion emission of Er<sup>3+</sup> ions in the Yb<sup>3+</sup>:Er<sup>3+</sup> co-doped systems has been well established in the literature<sup>12</sup>. The first IR photon excites the Yb<sup>3+</sup> ion to the 2F<sub>5/2</sub> level. The excitation may then relax radiatively back to the ground level (2F<sub>7/2</sub>). Alternatively, the energy can be transferred to the Er<sup>3+</sup> ion. This energy can promote the Er<sup>3+</sup> ion from the 2I<sub>15/2</sub> to the 2I<sub>11/2</sub> level, and if the latter is already populated a transition from the 2I<sub>11/2</sub> to the 2F<sub>7/2</sub> level can occur. The Er<sup>3+</sup> ion can relax nonradiatively to the 2H<sub>11/2</sub>, 4S<sub>3/2</sub> or 4F<sub>9/2</sub> levels. Therefore, both green (2H<sub>11/2</sub>, 4S<sub>3/2</sub> → 2I<sub>15/2</sub>) and red (2F<sub>9/2</sub> → 2I<sub>15/2</sub>) up-conversion emission is obtained.

The strongest up-conversion luminescence of the materials prepared with EDTA was obtained when the annealing temperature was 700 °C due to the large crystallite size (ca. 150 nm) and small surface area (Fig. 4). The smaller is the crystallite size the weaker is the total up-conversion luminescence due to the large surface area of the small particles. Large surface area increases the amount of the surface defects and the adsorption of the impurities (e.g. CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>3</sub>−) that weaken the luminescence. The luminescence of the as-prepared material and the material annealed at 200 °C are almost equally weak. This indicates that the crystallite sizes of the materials are the same, so the annealing temperature is too low to improve the up-conversion luminescence intensity.

![Figure 4. Up-conversion luminescence spectra of the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanomaterials annealed at selected temperatures (prepared with EDTA, left) and gas spheres (prepared without EDTA, right).](image)

The up-conversion luminescence spectra show that the emission bands have different shapes when annealed at different temperatures (Fig. 4). This is due to the different structures of the materials: the cubic and hexagonal forms have different crystal field affecting the Er<sup>3+</sup> luminescence centers. Also the low and high temperature cubic materials have different shape of the luminescence bands; this may suggest that the NaYF<sub>4</sub> has two different cubic structures.

When prepared without EDTA at 600 °C, the up-conversion luminescence of the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanomaterials was stronger than prepared with EDTA (Fig. 4) due to the efficiently luminescent hexagonal phase of the former material. When prepared with EDTA, there was cubic phase in the material that weakens the luminescence. Although the structure of the material annealed at 700 °C is cubic, the strong luminescence of the material is due to the large crystallite size.

The most intense luminescence of the materials prepared without EDTA and annealed at 600 °C was obtained with the inert N<sub>2</sub> gas sphere (Fig. 4, right). This is due to the lack of the color centers caused by oxygen in air or hydrogen in the N<sub>2</sub> + 10 % H<sub>2</sub> gas sphere. Especially when annealed in air, the color centers decreased the intensity of the green luminescence and increased the I<sub>red</sub>/I<sub>green</sub> ratio (Fig. 5).

When prepared with EDTA and annealed at 600 °C in N<sub>2</sub> + 10 % H<sub>2</sub>, the green luminescence was weaker compared to the materials prepared without EDTA (Fig. 5). This is probably due to EDTA that decreases the particle size and thus increases the surface area of the particles. The large surface area increases the amount of impurities (mainly OH) which causes the multiphonon de-excitation. Also the high I<sub>red</sub>/I<sub>green</sub> ratio at low annealing temperatures is due to the surface impurities of the small nanoparticles. The impurities weaken especially the green luminescence.
Conclusions

According to the FT-IR spectra there were no organic impurities due to EDTA in the NaYF₄:Yb³⁺,Er³⁺ nanomaterials. The metal-fluoride vibrations of the cubic and hexagonal phases could be observed in the FT-IR spectra. When the NaYF₄:Yb³⁺,Er³⁺ nanomaterials were prepared with EDTA, there was more cubic form than in the materials prepared without EDTA. This is probably due to the EDTA favoring the formation of the cubic form that usually possesses a smaller crystallite size than the hexagonal one. The heating temperature affected strongly the structure of the materials producing a cubic phase below 400, hexagonal between 400 and 600 and again a cubic one at 700 °C.

The NaYF₄:Yb³⁺,Er³⁺ nanomaterials produced very strong green and red up-conversion luminescence. The strongest total up-conversion luminescence was obtained from the material annealed at 700 °C due to the large crystallite size. The smaller is the crystallite size the larger is the surface area. Large surface area absorbs more (atmospheric) impurities which decreases the total up-conversion luminescence.

The high I_red/I_green ratio at low annealing temperatures is also due to the large surface area of the nanoparticles. This increases the amount of the surface impurities that weakens especially the green luminescence due to the multiphonon de-excitation mechanism. In the up-conversion luminescence spectra, the bands corresponding to different transitions of Er³⁺ have different shapes when annealed at different temperatures. This is due to the different structures of the materials: the cubic and hexagonal phases have different arrangement of anions, i.e. different crystal field, around the luminescence Er³⁺ centers. Also the low and high temperature cubic materials have different shapes of the luminescence bands; this may suggest that NaYF₄ has two different cubic structures.

Experimental Section

Synthesis. The nanocrystalline NaYF₄:Yb³⁺,Er³⁺ materials were prepared with the co-precipitation method. First, 2.1 g of NaF was dissolved in 60 cm³ of deionized water. Another aqueous solution was prepared by mixing together 16 cm³ YCl₃, 3.4 cm³ YbCl₃, 0.6 cm³ ErCl₃ and 20 cm³ EDTA solutions. The concentration of each solution was 0.2 moldm⁻³. The chloride-EDTA solution was poured into the NaF solution, and the mixture was stirred for 1 h at room temperature. Precipitate from the reaction was centrifuged, washed three times using deionized water and once with anhydrous ethanol. The precipitate was then dried under vacuum. Annealing of the nanomaterials was carried out under static gas sphere (N₂ + 10 % H₂, N₂ or air) by heating them to the desired temperature at a rate of 20 °C per minute, and maintaining this temperature for five hours. After annealing, they were cooled down freely to the room temperature under the same gas sphere. Selected materials were prepared without EDTA to study the effect of the chelating agent on the crystallite size and the up-conversion luminescence.

Characterization. The FT-IR spectra between 400 and 4000 cm⁻¹ were measured at room temperature with a Mattson Instruments GALAXY 6030 spectrometer. The material was mixed with KBr and then pressed to a transparent disc.

Thermal behaviour of the NaYF₄:Yb³⁺,Er³⁺ materials was studied with a TA Instruments SDT 2960 Simultaneous DTA-TGA apparatus between 25 and 1300 °C in a N₂ + 10 % H₂ gas sphere (flow rate:
100 cm⁻³min⁻¹). A heating rate of 10 °Cmin⁻¹ and sample weight of ca. 10 mg was used. Aluminium oxide sample pans and α-Al₂O₃ reference materials were used.

Crystal structures and phase purities of the materials were analyzed with the X-ray powder diffraction measurements. The patterns were collected at room temperature between 4 and 100° (in 2θ) with a Huber G670 image plate Guinier camera (CuKα₁ radiation, 1.5406 Å). The data collection time was 30 min.

The crystallite sizes of the NaYF₄:Yb⁺⁺,Er⁺⁺ materials were estimated from the diffraction data using the Scherrer formula (Eq. 1)[9]. In this equation, d is the mean crystallite size (m), λ the X-ray wavelength (m), β (rad) the full width at half maximum (FWHM) of the [111] reflection (2θ: 28.2°) for the cubic or the [101] reflection (2θ: 30.9°) for the hexagonal phase and θ (°) half of the Bragg’s angle (2θ). The reflection broadening due to the diffractometer was eliminated from the β-value by using a microcrystalline reference (βᵣ) (Eq. 2).

\[ d = \frac{0.9\lambda}{\beta \cos \theta} \] (1)

\[ \beta^2 = \beta^2 - \beta^2_r \] (2)

The up-conversion luminescence spectra of the nanomaterials were measured at room temperature with an Ocean Optics PC2000-CCD spectrometer. The spectral response of the spectrometer was calibrated with an Ocean Optics LS-1-CAL-INT calibration source. The NIR excitation (970 nm) source was a HTOE FLMM-0980-711-1300m fiber-coupled NIR laser diode (Hi-Tech Optoelectronics Co., Ltd). The laser diode was controlled with a Wavelength Electronics LDTC2/2 laser diode driver. There was a longpass filter (850 nm, Edmunds RG850) between the laser and the sample holder. The sample was inside a capillary tube. The emission was collected at a 90° angle to the excitation. A shortpass filter (850 nm, Edmunds 46386) between the sample holder and detector was used to exclude the exciting radiation from the detector. The emission was directed to the detector with an optical fiber (Ø 200 μm). Lenses were used to focus both the excitation and emission radiation. The spectra were collected with the Ocean Optics OOIrrad software.

**Acknowledgements**

Financial support from the Finnish Funding Agency for Technology and Innovation (Tekes) and the Graduate School of Materials Research (GSMR, Turku, Finland) for L.P. and from the Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM, Espoo, Finland) for I.H. is gratefully acknowledged. Ms. Maarit Myllykoski is acknowledged for assisting in the thermoanalytical measurements.
Unexpected sp$^3$ C-H Activation Upon Metallation of a New Cyclopentadienyl-N-silylphosphazene Ligand by the Yttrium Triaryl [Y(dmba)$_3$]

Nina Susanne Hillesheim and Jörg Sundermeyer*

Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Straße, D-35032 Marburg, Germany
E-mail: jsu@chemie.uni-marburg.de

Abstract. The reaction of cyclopentadienyl-phosphazenyl-silane C$_5$H$_4$SiMe$_2$N=P(NMe$_2$)$_3$ (1) with [Y(o-C$_6$H$_4$CH$_2$NMe$_2$)$_3$], abbreviated as [Y(dmba)$_3$], has been found to unexpectedly yield [{$\eta^5$:$\eta^1$-C$_5$Me$_4$SiMe$_2$N=P(NMe$_2$)$_2$(NMe-CH$_2$)}$\cdot$Y(o-C$_6$H$_4$CH$_2$NMe$_2$)] (4) containing the doubly deprotonated chelating ligand, as confirmed by 2D NMR spectroscopy and elemental analysis. The formation of 4 presumably proceeds via elimination of N,N-dimethylbenzylamine from an initially formed half-sandwich diaryl species 4'. Upon heating of 1 in benzene the quantitative formation of two equivalents of dimethybenzylamine was observed. Additionally the reaction of the potassium salt of the ligand (3) and [YCl(CH$_2$TMS)$_2$thf], formed in situ, yielded corresponding complex [{$\eta^5$:$\eta^1$-C$_5$Me$_4$SiMe$_2$N=P(NMe$_2$)$_2$(NMeCH$_2$)}-Y(CH$_2$TMS)(thf)] (5) again by metallation of one of the N-CH$_3$ substituents of the iminophosphorane functionality.

Keywords: Constrained Geometry Complexes; Functional Cyclopentadienyl Chelate Ligand; CH Activation; Rare-Earth Elements; Arene Elimination, Alkane Elimination.

Introduction

The development of constrained geometry catalysts (CGC) in the 1990s initiated an enormous improvement in the copolymerization of ethene with long-chain olefins.$^1$ In the classical dianionic CG ligand system a $\eta^3$-cyclopentadienyl and an amido group are bridged by a silanediyl (-SiMe$_2$-) moiety to form a constrained chelate ligand [CpSiN]$^2$ A. Recently we investigated four new monoanionic bidentate ligands [CpSiNP]$^1$ C and their lithium and potassium salts in which the amido moiety is substituted by a basic exocyclic phosphazene donor functionality.$^2$ They were established in a convergent multi-step synthesis and fully characterized. The unique property of these ligands is their ability to effectively delocalize a positive charge at the phosphorus atom, producing compounds with considerably enhanced basicity and nucleophilicity which can be described by two limiting resonance structures (CpSiMe$_2$N$^+$ versus CpSiMe$_2$N-P$^-$). The complexation of trivalent metal cations such as rare earth cations with ligands of type C should result in compounds isoelectronic (for R = CR$_3$ and group 3 metals) or in a more general aspect isolobal to group 4 CpSiN (A) complexes. Based on their isolobal relationship similar properties such as high activities in olefin polymerization catalysis should be expected. To our surprise, the protonated forms of ligands C proved to be unreactive towards metallation with various rare earth metal alkyls and amides. The remarkable low acidity of these ligands is in sharp contrast to the protic character of the cyclopentadienyl phosphazene ligands with an intracyclic phosphazene unit [CpPN]$^3$ B developed in our research group (Figure 1).$^1$ Due to the remarkably high basicity of type C ligands, the complexion of group 3 and 4 transition metals via amine or alkane elimination did not prove to be a feasible synthetic strategy for various alkyl and amido precursors.

Here we report that syntheses of the first metallated \( \text{CpSiNP} \) complexes of lanthanides were finally achieved applying the arene elimination pathway using chelate stabilized homo-leptic triaryl \( \text{[Y(dmba)3]} \)\(^4\) or applying a salt / alkane elimination strategy using alkyl complex \( \text{[Y(CH\text{TMS})2Cl(thf)}_n \).}

**Results and Discussion**

**Ligand synthesis**

The desired ligand was obtained in a two step synthesis. In the first step \( \text{LiC}_5\text{Me}_2\text{H}_4 \) was reacted with dichlorodimethylsilane to yield chloro-dimethyl-(2,3,4,5-tetramethyl-cyclopenta-2,4-dienyl)silane with only minor modifications to literature procedures.\(^3,7,8\) It is worth mentioning that just one regioisomer of the product is formed. The two other plausible cyclopentadienyl silane isomers could not be observed by NMR spectroscopy. The second step of the ligand synthesis involved the reaction of the chloro-dimethyl-cyclopenta-2,4-dienyl-silane with two equivalents of the commercially available tris(dimethylamino)-iminophosphorane.\(^9\) One equivalent of the iminophosphorane serves as a nucleophile, the other one acts as a supporting base and is transformed into the corresponding aminophosphonium chloride, which is formed as a stoichiometric by-product. Ligand \( \text{I} \) was obtained as a pale red air and water sensitive oil which was characterized by \(^1\text{H NMR}, ^{13}\text{C NMR} \) and \(^{31}\text{P NMR} \) spectroscopy, elemental analysis and by mass spectrometry (see experimental).

**Synthesis of \([\eta^5: \eta^1-\text{C}_5\text{Me}_5\text{SiNP(NMe}_2)_2]\text{(NMe}_2\text{-CH}_2)\text{Y(dmba)}\)] (4)**

Agostic interactions have been suggested as possible pre-transition states for C-H activation processes. Although agostic C-H interactions\(^10\) and C-H activations\(^11\) have often been reported for \( \text{d}^5 \) systems, the activation of particular agostic C-H bonds has been observed less frequently. Upon heating of \( \text{I} \) and \( \text{[Y(dmba)3]} \) in benzene at 80°C quantitative formation of two equivalents of \( \text{N, N-dimethylbenzylamine} \) and of \( \text{[(\eta^5: \eta^1-(C}_5\text{Me}_5\text{-SiMe}_2\text{N}=\text{P(NMe}_2)_2\text{(NMe}_2\text{-CH}_2)\})\text{Y}^{(\text{o-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)}\} \) was observed by NMR spectroscopy. The expected constrained geometry complex with the monoanionic ligand \( \text{I} \) \( \text{[(C}_5\text{Me}_5\text{SiMe}_2\text{N}=\text{P(NMe}_2)_2\})\text{Y(dmba)}\] was neither isolated nor observed spectroscopically as an intermediate. It is proposed, that for steric reasons an agostic C-H interaction followed by C-H activation of one of the NC-H bonds, and elimination of H(dmba) is favored instead of the formation of anticipated CG complex \( \text{4'} \).

---


The presence of a $sp^3$-carbon–yttrium bond in 4 was unambiguously established by NMR spectroscopic methods. The resonance due to the methylene moiety in the $^1H$ NMR spectrum shows the distinctive coupling pattern expected for a direct Y–C bonding interaction of the methylene carbon atom. Each resonance of the diastereotopic protons of the N-CH$_2$-Y unit appears as a ddd pattern with coupling constants of $^2J_{LY} = 1.83$ Hz, $^3J_{LY} = 16.5$ Hz and $^2J_{HH} = 10.6$ Hz. At this stage we only can speculate, that the ligand regime at yttrium is completed by a weak phosphaene N-Y bond.

**Synthesis of [[η²:η¹-C$_5$Me$_5$SiMe$_5$N=P(NMe$_2$)$_2$(NMe-CH$_2$)] Y(CH$_3$TMS)(thf)] (5)**

As a different synthetic approach to anticipated constrained geometry complexes with ligand 1 a salt metathesis reaction was investigated. The lithium salt 2 of ligand 1 was synthesized by reacting N-silylphosphaene 1 with nBuLi in hexane. The lithium salt is insoluble in hexane, toluene and benzene, but partially soluble in THF. As the salt metathesis of 2 and [Y(CH$_3$TMS)$_2$Cl(thf)$_3$], formed *in situ*, proved to exhibit low selectivity towards the desired product, we decided to use potassium salt 3 instead. 3 was synthesized by reaction of 1 with benzyl potassium in Et$_3$O, isolated and characterized. After generating [Y(CH$_3$TMS)$_2$Cl(dme)] *in situ*, it was transformed in the presence of 3 into a product with a single resonance in the $^{31}$P NMR spectrum at 36.8 ppm splitting in a doublet with a coupling constant of $^3J_{YP} = 5.8$ Hz. $^1$H, $^{13}$C and 2D NMR spectra are fully consistent with the structure of 5.

Again the same reaction pattern was observed: Instead of forming the desired CG complex 5', a double deprotonation at ligand 1 was the result of a C-H activation process. A literature survey reveals, that most alkane, arene and amine elimination reactions of homoletic RE trisalkyls/amides with protonated ligands lead to the expected mono-metallated ligand complexes. Only a few reports of further C-H activation of an NMe$_2$ unit linked to a cyclopentadienyl or benzyl fragment appeared to yield N-CH$_2$-M structural motives.$^{[12]}$ One of the examples is the thermolysis of [Cp$'$Y(o-C$_6$H$_4$CH$_2$NMe$_2$)$_2$] to [Cp$'$Y(o-C$_6$H$_4$CH$_2$NMe(CH$_2$-µ))($µ$-o-C$_6$H$_4$CH$_2$(NMe-CH$_2$))YCp$^*$](thf)] and N,N-dimethylbenzylamine observed by Teuben.$^{[13]}$

In summary, a new phosphazenylsilane functionalized cyclopentadienyl ligand 1 and its anionic lithium (2) and potassium (3) salt has been introduced. The chemistry of this ligand with yttrium alkyl and aryl precursor complexes is dominated however by C-H activation and a second deprotonation / metallation of the NCH$_2$ functional groups leading to a rather unusual stericly more relaxed (not constrained) ligand system in 4 and 5.

To the best of our knowledge this is the first example of a C-H activation of a RN=P(NMe$_2$)$_2$ unit in the presence of a rare earth metal alkyl or aryl. The only related reaction is the deprotonation of the related HMPT O=P(NMe$_2$)$_2$ to the metalated O=P(NMe$_2$)$_2$NMeCH$_2$Li.$^{[14]}$

---


Experimental Section

All operations were performed in a glovebox under a dry dinitrogen atmosphere (MBraun 150 BG-I) or at a vacuum line using Schlenk techniques. Solvents were purchased from Fluka, Aldrich, Acros and Merck and used after drying and purification according to generally used methods under inert atmosphere. After pre-desiccation and distillation the solvents were stored in absorption columns over Al₂O₃/molecular sieve 3Å/R3-11G-catalyst (BASF). The rare earth chloride [YCl₃·6H₂O] was prepared by dissolving [Y₂O₃] in conc. hydrochloric acid (p.a.) followed by evaporation. 1,2-dimethoxyethane (DME), diethyl ether, THF, hexane, benzene and toluene were purified by conventional methods. Rare earth metal content in solvated lanthanide trichlorides was determined by complexometric titration with EDTA in the presence of xylene orange as indicator. The following compounds were synthesized according to literature procedures: Li(dmba), [Y(dmba)₃], [YCl₃(dme)]₂, N,N-dimethylbenzylamine. Benzylamine and nBuLi (1.6 M solution in hexane) were used as supplied (Acros, Chemetall).

1H, 13C and 31P NMR spectra were recorded on Bruker ARX 200 or AC 300 and DRX 500 spectrometers. Small amounts of non deuterated solvent were used for calibration of 1H and 13C NMR spectra. 1H, 13C and 31P chemical shifts are expressed with a positive sign, in parts per million, relative to external SiMe₄ and 85% H₃PO₄. Unless stated otherwise NMR spectra were recorded at 293 K. The assignment of all resonances was supported by two-dimensional NMR spectroscopy (COSY, HMOC and HMBC experiments). Electron impact mass spectra (EI-MS) were taken on a Varian CH7A at 70 eV. Elemental analysis samples were prepared from repeatedly recrystallized material and were carried out on a Heraeus CHN rapid analyzer. Nevertheless all of the organo yttrium complexes proved to be too air sensitive to get fully satisfactory elemental analysis or HRMS data. Due to yttrium (silicon) carbide formation carbon contents tend to be lower as calculated.

Synthesis of the ligand and its potassium and lithium salt

Synthesis of tris-P-dimethylamino-N-[dimethyl-(2,3,4,5-tetramethyl-cyclopenta-2,4-dienyl)-silanyl]-phosphazen, C₅Me₅H₅SiMe₅N=P(NMe₃)₃ (1)

To a stirred suspension of hexamethyldiamino-iminophosphorane (0.9 mL, 5.0 mmol, 2.0 eq) in 15 mL toluene and chloro-dimethyl-(2,3,4,5-tetramethyl-cyclopenta-2,4-dienyl)silane (540 mg, 2.5 mmol, 1.0 eq) was added at 0°C. The suspension was warmed up to ambient temperature over night and stirred for 16 h. The color of the reaction mixture slowly turned yellowish whereupon [NH₃P(NMe₃)₃]⁺Cl⁻ precipitated. The solution was filtered off and washed twice with hexane and the solvent was removed from the filtrate under reduced pressure. A pale reddish oil was obtained in 82% yield (745 mg, 2.04 mmol). The product is miscible with hexane, benzene und toluene.

CHN: C₅H₁₀SiNP: calc.: C: 57.26, H: 10.46, N: 15.71; found: C: 56.37, H: 10.59, N: 16.64. 1H-NMR (CD₃O, 300.1 MHz): δ/ppm = 3.05 (s, 1 H, CH₂), 2.37 (d, 3JCH =10.3 Hz, 18 H, (NCH₃)₂), 2.26 (s, 6 H, CH₂C(CH₃)₂), 1.95 (s, 6 H, CH₂C(CCH₃)₂), 0.24 (s, 6 H, Si(CH₃)₃). 13C-NMR (CD₃O, 75.5 MHz): δ/ppm = 134.2 (C₅), 134.1 (C₅), 59.7 (d, 3JC₂ = 4.6 Hz, CH₂), 73.7 (d, 3JC₅ = 3.5 Hz, N(CH₃)₂), 15.0 (HC-C(CH₃)₃), 11.6 (HC-C(CCH₃)₂), 2.83 ((CH₃)₃Si). 31P-NMR (CD₃O, 81.0 MHz): δ/ppm = 14.9. EI/MS m/z (%) = 356 (1.0) [M⁺], 298 (1.0) [M-4 CH₂+H⁺], 235 (66.8), 192 (100.0) [SiC₅N₅PN(CH₃)₂+H⁺], 149 (46.7) [SiC₅N₃P+H⁺], 102 (20.8) [SiC₅N⁺], 59 (5.4) [Si(CH₃)₂+H⁺], 44 (18.9) [N(CH₃)₃]⁺.

Synthesis of lithium salt Li(C₅Me₅H₅SiMe₅N=P(NMe₃)₃) (2)

To a stirred solution of 1 (713 mg, 2.0 mmol) in 15 mL hexane 0.8 mL of a nBuLi-solution (2.5 M in hexane) were added dropwise at -78°C. The suspension was stirred over night and was allowed to warm up to ambient temperature. The precipitate was separated by filtration, washed twice with 8 mL hexane and dried under reduced pressure. 2 was obtained as a colorless solid in 44% yield (322 mg, 0.89 mmol).

CHN: C₅H₁₀SiNP:Li: calc.: C: 56.33, H: 10.01, N: 15.46; found: C: 55.39, H: 10.85, N: 16.88. 1H-NMR (d₅THF, 300 MHz): δ/ppm = 2.57 (d, 3JCH = 10.2 Hz, 18 H, (NCH₃)₂), 1.98 (s, 6 H, CH₂C(CH₃)₂), 1.75 (s, 6 H, CH₂C(CCH₃)₂), -0.10 (s, 6 H, SiCH₃). 13C-NMR (d₅THF, 75.5 MHz): δ/ppm = 37.5 (C₅H₅), 15.0 (HC-C(CH₃)₃).


© 2010 NWT-Verlag, Bornheim, Germany
11.2 (CH_{2}C=CHCH_{2}). 0.7 (Si(CH_{3})_{2}). The signals of the quaternary carbon atoms of the (C_{5}Me_{5}) ring could not be detected. \textsuperscript{31}P-NMR (d\textsuperscript{6}THF, 81.0 MHz): \delta/ppm = 15.6. EI/MS m/z (%) = 356 [M-Li]+, 298 [M-4 CH_{2}+H]+, 235, 192 [SiC_{4}N_{3}P(N(CH_{3})_{2})+H]+, 149 [SiC_{4}N_{3}P+H]+, 102 [SiC_{4}N]+, 59 [Si(CH_{3})_{2}+H]+, 44 [N(CH_{3})_{2}]\textsuperscript{+}. 

**Synthesis of potassium salt K(C_{5}Me_{5}SiMe_{2}N=P(NMe\textsubscript{2})\textsubscript{2}X)(3)**

To a stirred solution of 1 (1.78 g, 5.0 mmol) in 25 mL Et\textsubscript{2}O 0.65 g of benzyl potassium was added at -78°C. A reddish suspension was formed. The suspension was stirred over night and was allowed to warm up to ambient temperature. The volatile components were removed under reduced pressure. The residue was suspended in hexane. The precipitate was separated by filtration, washed twice with 8 mL hexane and dried in vacuo. 3 was obtained as a colorless solid in 45% yield (893 mg, 2.26 mmol).

**CHN**: C\textsubscript{47}H\textsubscript{50}N\textsubscript{5}P\textsubscript{2}K: calc.: C: 47.9, H: 4.6, N: 11.5; found: C: 47.5, H: 4.7, N: 11.3.

**Synthesis of [(C\textsubscript{5}Me\textsubscript{5}SiMe\textsubscript{2}N=P(NMe\textsubscript{2})\textsubscript{2}NMe\textsubscript{2}-CH\textsubscript{2})](4)**

[Y(dmba)\textsubscript{3}] (305 mg, 0.62 mmol) and 1 (171 mg, 0.48 mmol) were dissolved in 12.0 mL of benzene. The solution was stirred at 80°C over night. Benzene and dimethylbenzylamine were removed at 40°C under reduced pressure. The brown residue was suspended in 5 mL of hexane. The suspension was stored at -30°C over night prior to centrifugation. The solution was decanted and the beige solid was washed with pentane and dried in vacuo.

**CHN**: C\textsubscript{62}H\textsubscript{64}N\textsubscript{6}P\textsubscript{2}SI: calc.: C: 47.9, H: 3.5, N: 14.8; found: C: 47.5, H: 3.5, N: 14.7.

**Synthesis of [(C\textsubscript{5}Me\textsubscript{5}SiMe\textsubscript{2}N=P(NMe\textsubscript{2})\textsubscript{2}NMe\textsubscript{2}-CH\textsubscript{2})Y(THF)TMS](thf)(5)**

To a stirred solution of 1 (356 mg, 1.0 mmol) in 10 mL of THF benzyl potassium (130 mg, 1.0 mmol) was added at -78°C. The potassium salt 1 was suspended in THF at 0°C. In a separate flask [YCl\textsubscript{4}(dme)\textsubscript{2}] (375 mg, 1.0 mmol) and LiCH\textsubscript{2}TMS (188 mg, 2.0 mmol) were mixed as solids and suspended at 0°C in THF. Both suspensions were stirred for an additional hour, then the [YCl\textsubscript{4}(dme)\textsubscript{2}] / LiCH\textsubscript{2}TMS suspension was added to the potassium salt suspension via a cannula at -78°C. The precipitate gradually disappeared, and the solution was allowed to warm to room temperature during 1 h. The volatile components were removed under reduced pressure, leaving a white solid suspended in a yellow oil which was extracted with hexane. Filtration and removal of all volatile components from the filtrate under reduced pressure yielded the product as a foamy white solid.

**CHN**: C\textsubscript{69}H\textsubscript{67}N\textsubscript{7}P\textsubscript{2}SI\textsubscript{2}Y: calc.: C: 48.4, H: 3.6, N: 13.4; found: C: 48.2, H: 3.6, N: 13.3.

**Acknowledgements**

Financial support by Deutsche Forschungsgemeinschaft (Priority Program 1166) is gratefully acknowledged. We also thank Chemetall GmbH, Frankfurt a.M. for the donation of lithium alkyls and for financial support.
Dicyanonitrosomethanide and Carbamoylcyanonitrosomethanide: Heterofunctionalised Anionic Ligands for the Formation of 3d/4f Bimetallic Coordination Polymers and Complexes

Anthony S. R. Chesman, David R. Turner, Glen B. Deacon, Stuart R. Batten*

School of Chemistry, Monash University, Victoria 3800, Australia
E-mail: stuart.batten@sci.monash.edu.au

Abstract. The two-dimensional heterobimetallic coordination network [[Na(H2O)3][Ce(dcnm)4(H2O)4]] (dcnm = dicyanonitrosomethanide) was obtained from an aqueous reaction of Na(dcnm) and CeCl3·7H2O. The structure contains \(\mu_2^{\eta_2}\eta_1\) nitroso-bridged Ce-Na pairs. These heterometallic units are joined through non-chelating dcnm ligands, via nitrile-Na and O-Ce interactions, to produce (4,4) sheets. The transition metal promoted \textit{in situ} nucleophilic addition of water to dcnm results in the formation of carbamoylcyanonitrosomethanide (ccnm) which is included in the trinuclear 3d/4f heterobimetallic complex \([\text{Gd(OH)}(ccnm)_2(H_2O)_4]_2\text{Mn}^{\text{III}}(\text{ClO}_4)_3\cdot2(18\text{-crown-6})\), which formed from an aqueous reaction of Gd(dcnm)3, Mn(ClO4)2·6H2O and 18-crown-6. The ccnm ligands display a \(\mu_2^{\eta_2}(\text{O}_\text{carbamoyl},\text{N}_\text{nitroso})\text{Gd}:\eta_1(\text{O}_\text{nitroso})\text{Mn}\) coordination mode, with the 18-crown-6 molecules residing in the lattice acting as hydrogen bond acceptors to aqua and ccnm ligands, resulting in the formation of (4,4) sheets.

Keywords: Heterobimetallic; Dicyanonitrosomethanide; Self Assembly; Hydrogen bonding

Introduction

The polynitrile anions dicyanamide and tricyanomethanide are widely recognised for their ability to form coordination polymers of varying dimensionalities, which may often display interesting magnetic properties such as long range ferromagnetic coupling.\(^1\) However, the homofunctionalised nature of these ligands may create difficulties in forming complexes which incorporate different metal types, as the nitrile groups will preferentially coordinate to specific metals, creating only homometallic systems. In order to overcome these synthetic challenges, related heterofunctionalised ligands such as dicyanonitrosomethanide (dcnm)\(^5\) and carbamoyldicyanomethanide (cdm),\(^3\) offer a means of utilising functional groups that target specific metal types, creating bimetallic systems. In addition to the rich variety of coordination modes offered by the dcnm ligand,\(^4,5,6,7,8,9,10\) it has also shown a propensity to undergo the \textit{in situ} transition metal promoted nucleophilic addition of water,\(^11\) protic solvents\(^12,13\) or amines\(^14\) to a nitrile group, giving rise to a diverse range of derivative

---

Ligands (Figure 1). The acid-catalysed addition of amines and alcohols to dicyanonitrosomethanide is also known, although this reaction pathway results in the protonation of the nitroso functional group, forming an oxime.\(^\text{15}\)

![Diagram of ligand structures and their reactions](image)

**Figure 1.** Ligands resulting from nucleophilic addition to dcnm; TM = transition metal (en = 1,2-diaminoethane, pn = 1,3-diaminopropane).

The addition of water or methanol to the dcnm ligand results in the formation of carbamoylecyananitrosomethanide (ccnm) and cyano(imino(methoxy)methyl)nitrosomethanide (cmnm), respectively. These ligands have demonstrated versatility in forming complexes of varying nuclearity, with the ccnm ligand being incorporated into polycarbonatolanthanide clusters known as 'lanthaballs', \([\text{Ln}_n\text{(H}_2\text{O})_m\text{(phen)}_n\text{(ccnm)}_6\text{(CO}_3\text{)}_{12}]\cdot\text{Cl}_3\cdot\text{CO}_3\)\(^\text{16}\), while the cmnm ligand can be found in the antiferromagnetically coupled trinuclear \([\text{Mn}^{II}_2\text{Mn}^{III}\text{(cmnm)}_3]\text{(NO}_3\text{)}\cdot2\text{H}_2\text{O}\)\(^\text{17}\) or the solvothermally synthesised, ferromagnetically coupled, coordination polymer \([\text{Cu(cmnm)}_2]\)_\(^\text{18}\). Despite the potential offered by these ligands in forming heterobimetallic complexes, to the best of our knowledge only one such complex exists, \([\text{Na(H}_2\text{O)}_6]\cdot[\text{Ni}_2\text{Na(ccnm)}_6]\)_\(^\text{19}\). In this complex the ccnm displays a \(\mu_2\eta^2\text{(O}_{\text{carbamoyl}},\text{N}_{\text{nitroso}})\text{Ni}\eta^1\text{(O}_{\text{nitroso}})\text{Na}\) coordination mode, demonstrating the potential of this ligand system for further heterobimetallic application.

---

Herein we report the crystal structures of the first heterobimetallic coordination polymer and discrete 3d/4f bimetallic complex to incorporate the dcnm and ccnm ligands, respectively.

Results and Discussion

The reaction of Na(dcnm) with CeCl$_3$·7H$_2$O in methanol afforded upon evaporation to dryness a small number of pale yellow crystals of the complex [[Na(H$_2$O)$_3$][Ce(dcnm)$_4$(H$_2$O)$_4$]] (1), sufficient in quantity for only infra-red spectroscopy and single crystal X-ray diffraction analysis. The compound crystallises in the non-centrosymmetric orthorhombic space group $Ih'$. The asymmetric unit contains one half of a unique Ce atom, one half of a unique of Na atom, two unique dcnm ligands (type I and II, Figure 2a), and four unique aqua ligands (two of which bind to Ce, and two of which bind to Na). The repeating chemical unit of the structure is [[Na(H$_2$O)$_3$][Ce(dcnm)$_4$(H$_2$O)$_4$]], consisting of a [Ce(dcnm)$_4$(H$_2$O)$_4$]$^-$ moiety which is charged-balanced by a partially hydrated sodium ion (Figure 2a). The cerium atom is 10-coordinate with two $\eta^2$-chelating type I dcnm ligands, two O-donor type II dcnm ligands, and four water molecules in the coordination sphere. The coordination geometry of the cerium atom can be described as square-antiprismatic if the chelating ligands are viewed as being monodentate from the N=O midpoint. The chelating nitroso group is unusual for the dcnm ligand, although we have previously observed this coordination mode with rare-earths in structures of the form $(R_4N)_3[Ln(dcnm)]_3$.$^5$ The chelation in the current study is not as symmetrical as that observed in the $[Ln(dcnm)]_3^-$ systems, with the difference between the Ce–O and Ce–N bond lengths being 0.242(11) Å, compared to less than 0.05 Å in the discrete [Ce(dcnm)$_4$]$^-$ complexes.$^5$ The chelating type I dcnm ligand is also involved in a bridging interaction to the sodium ion through the oxygen atom, making the full coordination mode of the ligand $\mu_2-\eta^1$O,N,Ce-$\eta^1$O,Na. The oxygen atom is situated almost centrally between the cerium and sodium atoms with bond lengths of 2.497(5) and 2.389(6) Å, respectively. The sodium atom is 7-coordinate with interactions to two type I dcnm oxygen atoms, two type II dcnm nitrile nitrogen atoms and three aqua ligands, and adopts a distorted mono-capped trigonal-prismatic coordination geometry (Figure 2b).

![Figure 2.](image-url)
**Table 1.** Selected bond lengths (Å) and angles (°) for 1.

<table>
<thead>
<tr>
<th>Bond/Distance</th>
<th>Value</th>
<th>Bond/Distance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(1)–O(1)</td>
<td>2.497(5)</td>
<td>Ce(1)–O(2)</td>
<td>2.455(5)</td>
</tr>
<tr>
<td>Ce(1)–N(1)</td>
<td>2.739(6)</td>
<td>Ce(1)···N(4)</td>
<td>3.108(5)</td>
</tr>
<tr>
<td>Ce(1)–O(3)</td>
<td>2.608(4)</td>
<td>Ce(1)–O(4)</td>
<td>2.593(5)</td>
</tr>
<tr>
<td>Na(1)–O(1)</td>
<td>2.389(6)</td>
<td>Na(1)–N(5)</td>
<td>2.587(6)</td>
</tr>
<tr>
<td>Na(1)–O(5)</td>
<td>2.303(6)</td>
<td>Na(1)–O(6)</td>
<td>2.398(12)</td>
</tr>
<tr>
<td>Ce(1)···Na(1)</td>
<td>3.919(4)</td>
<td>O(1)–N(1)</td>
<td>1.313(7)</td>
</tr>
<tr>
<td>Ce(1)–O(1)–N(1)</td>
<td>86.0(4)</td>
<td>Ce(1)–O(1)–Na(1)</td>
<td>106.6(2)</td>
</tr>
<tr>
<td>O(3)···N(3)%</td>
<td>2.849(6)</td>
<td>O(4)···N(6)*</td>
<td>2.871(6)</td>
</tr>
</tbody>
</table>

* Symmetry elements used: % = ½ + x, ½ – y, z; * = x – ½, ½ – y, z.

**Figure 3.** (a) The Na/Ce units act as the 4-connecting nodes in the (4,4) network. (b) One (4,4) sheet as viewed looking down the b-axis.

Only two of the nitrile groups per [NaCe(dcnnm)_4(H_2O)_7] unit (out of a total of eight) are involved in coordinative bonding to metal atoms. Although the hydrogen atoms of the aqua ligands could not be crystallographically located, the interatomic distances between the nitrogen atom of one nitrile group of each of the two unique dcnnm ligands and the oxygen atoms of two coordinated water molecules are suggestive of hydrogen bonding (Table 1). The remaining nitrile substituents not participating in any coordinative or hydrogen bonding are directed parallel to the 2D sheets of the (4,4)-network.

An aqueous solution of Mn(ClO_4)_2·6H_2O, 18-crown-6 and Gd(dcnm)_3 was allowed to evaporate to dryness, yielding a small number of crystals of the complex [(Gd(OH)(ccnm)_2(H_2O)_4) Mn^{III}](ClO_4)_2·2(18-crown-6) (2), insufficient in quantity for additional analysis. The ccnm ligand results from the manganese ions promoting the nucleophilic addition of water to a nitrile group of dcnn to form a carbamoyl group, as has been observed with
The product crystallises in the monoclinic space group $C2/c$, with the asymmetric unit containing one unique half of the $\left[\text{Gd(OH)}(\text{ccnm})_2(\text{H}_2\text{O})_4\right]^{2+}$ complex, one 18-crown-6 molecule, one complete and one half occupancy perchlorate anion and several partial occupancy water molecules disordered throughout the lattice. The $\left[\text{Gd(OH)}(\text{ccnm})_2(\text{H}_2\text{O})_4\right]^{2+}$ complex consists of two $\left[\text{Gd(OH)}(\text{ccnm})_2(\text{H}_2\text{O})_4\right]^{2+}$ moieties which bridge through the hydroxide group and the nitroso groups of the two ccnm ligands to the central manganese atom. The ccnm ligands chelate to the gadolinium atom via the oxygen and nitrogen atoms of the carbamoyl and nitroso groups, respectively, resulting in a $\mu_2$-$\eta^2$(O$_{\text{carbamoyl}},\eta_1^1$(O$_{\text{nitroso}}$))Gd: $\eta^1$(O$_{\text{nitroso}}$)Mn coordination mode. The two unique ccnm ligands coordinate in a cis fashion to one face of the metal centre, with the four aqua ligands and the bridging hydroxide group coordinating on the opposite side of the metal centre (Figure 4, Table 2).

![Figure 4.](image)

**Figure 4.** (a) The $\left[\text{Gd(OH)}(\text{ccnm})_2(\text{H}_2\text{O})_4\right]^{2+}$ complex. Ellipsoids shown at 50 % probability, symmetry element used: $\dagger = \frac{1}{2} - x, \frac{1}{2} - y, -z$. (b) The coordination mode of the ccnm ligand.

**Table 2.** Selected bond lengths (Å) and angles (°) for 2.$^a$

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd(1)–N(1)</td>
<td>2.604(5)</td>
</tr>
<tr>
<td>Gd(1)–O(2)</td>
<td>2.418(5)</td>
</tr>
<tr>
<td>Gd(1)–N(4)</td>
<td>2.643(6)</td>
</tr>
<tr>
<td>Gd(1)–O(4)</td>
<td>2.436(5)</td>
</tr>
<tr>
<td>Gd(1)–O(5)</td>
<td>2.331(5)</td>
</tr>
<tr>
<td>Gd(1)–O(6)</td>
<td>2.446(5)</td>
</tr>
<tr>
<td>Gd(1)–O(7)</td>
<td>2.417(5)</td>
</tr>
<tr>
<td>Gd(1)–O(8)</td>
<td>2.414(5)</td>
</tr>
<tr>
<td>Gd(1)–O(9)</td>
<td>2.456(5)</td>
</tr>
<tr>
<td>Gd(1)–Mn(1)</td>
<td>3.7427(3)</td>
</tr>
<tr>
<td>Mn(1)–O(3)</td>
<td>2.070(5)</td>
</tr>
<tr>
<td>Mn(1)–O(5)</td>
<td>1.882(5)</td>
</tr>
<tr>
<td>N(1)–Gd(1)–O(2)</td>
<td>63.2(2)</td>
</tr>
<tr>
<td>N(4)–Gd(1)–O(4)</td>
<td>62.4(2)</td>
</tr>
<tr>
<td>O(1)–Mn(1)–O(3)</td>
<td>89.6(2)</td>
</tr>
<tr>
<td>O(1)–Mn(1)–O(5)</td>
<td>90.3(2)</td>
</tr>
<tr>
<td>O(1)–Mn(1)–O(3)$^\dagger$</td>
<td>90.4(2)</td>
</tr>
</tbody>
</table>

$^a$Symmetry element used: $\dagger = \frac{1}{2} - x, \frac{1}{2} - y, -z$.

The coordination geometry of the 9-coordinate gadolinium atoms can be best described as monocapped square antiprismatic with the central manganese atom having an octahedral geometry. The 3+ oxidation state of manganese is confirmed by bond valence sum calculations and is also supported by the charge balancing of the complex by the perchlorate anions in the lattice.

Although hydrogen atoms of the aqua ligands could not be located by X-ray crystallography, the bond lengths and the angle between two oxygen atoms of the 18-crown-6 molecule and the water molecule coordinated to the gadolinium atom in the capping position of the monocapped square antiprismatic are strongly suggestive of hydrogen bonding (O(6)–O(13) = 3.000(7), O(6)–O(13)–O(10) = 109.8(2)). The hydroxide which bridges the manganese and gadolinium metal centres is orientated so it also acts as a hydrogen bond donor to the same 18-crown-6 molecule. Additionally, the carbamoyl group of one unique ccnm ligand also forms hydrogen bonds to an adjacent 18-crown-6 molecule (Figure 5, Table 3). Each $\left[\text{Gd(OH)}(\text{ccnm})_2(\text{H}_2\text{O})_4\right]^{2+}$·2(18-crown-6) hydrogen bonded unit forms hydrogen bonds to four other equivalent units, resulting in the formation of a hydrogen bonded (4,4) network. Vacant crown molecules have
previously been observed to act as versatile hydrogen bond acceptors, with numerous examples of aqua ligands hydrogen bonding to 12-crown-4,\textsuperscript{20} 15-crown-5,\textsuperscript{21,22} and 18-crown-6\textsuperscript{23} to form 1D chains. The carbamoyl group of the unique ccnm ligand which is not participating in hydrogen bonding to the 18-crown-6 molecule acts as a hydrogen bond donor to the full occupancy perchlorate anion and a water molecule residing in the lattice (Table 3).

Figure 5. (a) A \{[Gd(OH)(ccnm)$_2$(H$_2$O)$_4$]Mn\}$^{18}$ complex from 2 hydrogen bonding to four adjacent 18-crown-6 molecules. Symmetry elements used: † = $\frac{1}{2} - x$, $\frac{1}{2} - y$, $-z$; ‡ = $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$. (b) One (4,4) sheet as viewed looking down the crystallographic $a$-axis.

Table 3. Hydrogen bond lengths and angles in 2.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(6)--O(10)</td>
<td>2.930(8)</td>
<td>175.2</td>
</tr>
<tr>
<td>N(6)--O(13)</td>
<td>3.072(8)</td>
<td>152.1</td>
</tr>
<tr>
<td>N(3)--O(19)</td>
<td>2.995(11)</td>
<td></td>
</tr>
<tr>
<td>N(3)--O(24)</td>
<td>2.872(8)</td>
<td>146.3</td>
</tr>
<tr>
<td>O(6)--O(10)</td>
<td>3.032(7)</td>
<td></td>
</tr>
<tr>
<td>O(6)--O(13)</td>
<td>3.000(7)</td>
<td>109.8(2)</td>
</tr>
</tbody>
</table>

* Symmetry elements used: \( \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z \).

Conclusion

The heterofunctionalised ligand dcnm and its water addition derivative ccmn have proven to be viable ligands in the formation of bimetallic polynuclear complexes and coordination polymers. The 2D sheet \([Na(H_2O)_3][Ce(dcnm)_4(H_2O)_4]\) marks substantial progress towards the formation of 3d/4f pseudohalide based coordination polymers while \([Gd(OH)(ccmn)_2(H_2O)_4]_2Mn^{10}\)(ClO_4)_3 demonstrates the ability of this class of ligands to form heterometallic discrete clusters. Future work will focus upon utilising these ligand systems, specifically exploiting the in situ nucleophilic addition of alcohols and amines to dcnm, for the formation of coordination polymers of novel connectivity and increasing the nuclearity of the resultant polynuclear clusters with a view to examine the novel magnetic properties that may arise.

Experimental Section

General

All reactions were carried out under aerobic conditions using commercial grade reagents. Ag(dcnm) was synthesised according to literature procedure. Infrared data were collected using a Perkin Elmer ATR-FTIR spectrometer.

Synthesis

\([NaCe(dcnm)_4(H_2O)_7]\) (1)

CeCl_3·7H_2O (53 mg, 142 \(\mu\)mol), Mn(ClO_4)_2·6H_2O (36 mg, 134 \(\mu\)mol) and Na(dcnm) (50 mg, 427 \(\mu\)mol) were dissolved in methanol (7 ml) and the reaction solution was allowed to evaporate to dryness over a period of one week, resulting in the formation of several isolated orange crystals of 1 amongst an amorphous precipitate. IR (ATR): \(\nu = 3196 \text{ (m, br)}, 2229 \text{ (m)}, 1620 \text{ (vw)}, 1484 \text{ (s)}, 1414 \text{ (m)}, 1268 \text{ (w)}, 1196 \text{ (s)}, 949 \text{ (m)} \text{ cm}^{-1}\).

\([Gd(ccmn)_2(OH)(H_2O)_4]_2Mn(ClO_4)_2(2\text{-18-crown-6})\cdot8.4(H_2O) \) (2)

Ag(dcnm) (70 mg, 347 \(\mu\)mol) was added to a solution of GdCl_3·6H_2O (43 mg, 116 \(\mu\)mol) dissolved in water (4 ml). The reaction solution was stirred while covered from light for one hour and then filtered to remove the precipitate of AgCl. Mn(ClO_4)_2·4H_2O (30 mg, 112 \(\mu\)mol) and 18-crown-6 (31 mg, 117 \(\mu\)mol) were dissolved in the reaction solution which was then allowed to evaporate to dryness, resulting in the formation of several isolated crystals of 2 amongst an amorphous precipitate.

Crystallographic details and data

A single crystal was mounted on fine glass fibres using viscous hydrocarbon oil. Data were collected on a Nonius KappaCCD (1) or Bruker X8 Apex II CCD (2) diffractometer, both equipped with graphite monochromated Mo-K\(\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)). The data collection temperature was maintained at 123 K using an open-flow N\(\text{2}\) cryostream. For data collection on a Nonius KappaCCD diffractometer integration was carried out by the program DENZO-SMN and data were corrected for Lorentz-polarisation effects and for absorption using the program SCALEPACK. For data collection on a Bruker X8 Apex II diffractometer integration and initial processing was carried out using the SAINT program suite and data was corrected for Lorentz-polarization effects and for absorption. The structures were solved by direct methods using SHELXS-


followed by successive refinements using full matrix least squares against $F^2$ using SHELXL-97. The program X-Seed was used as a graphical SHELX interface. X-ray data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 758816 (1), 758817 (2)).

$$\text{[[NaCe(dcm)$_4$(H$_2$O)$_7$]] (1): C$_{12}$H$_{14}$CeN$_{12}$NaO$_{11}$, } M = 665.46,$$

ortherhombic, space group $Aba2$ (No. 41), $a = 6.7903(2)$, $b = 19.1564(4)$, $c = 18.5410(4)$ Å, $V = 2411.77(10)$ Å$^3$, $Z = 4$, $D_\text{c} = 1.833$ g/cm$^3$, $F_{000} = 1308$, 12228 reflections collected, 1436 unique ($R_{\text{int}} = 0.0765$). Final $GooF = 1.077$, $R1 = 0.0379$, $wR2 = 0.0980$, $R$ indices based on 1224 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 169 parameters, 1 restraint. Lp and absorption corrections applied, $\mu = 1.983$ mm$^{-1}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the aqua ligands could not be accurately located from the Fourier difference map. The structure was refined as a racemic twin.

$$\text{[[Gd(ccnm)$_2$(OH)(H$_2$O)$_{12}$]Mn(ClO}_4)]_22(18\text{-crown-6})\cdot8.4(H$_2$O) (2): C$_{36}$H$_{90.80}$Cl$_2$Gd$_2$MnN$_{12}$O$_{50.40}$, } M = 1974.20,$$

red shard, $0.20 \times 0.10 \times 0.10$ mm$^3$, monoclinic, space group $C2/c$ (No. 15), $a = 23.7186(7)$, $b = 17.4867(6)$, $c = 20.0697(5)$ Å, $\beta = 110.115(2)^\circ$, $V = 7816.4(4)$ Å$^3$, $Z = 4$, $D_\text{c} = 1.678$ g/cm$^3$, $F_{000} = 3992$, $2\theta_{\text{max}} = 55.0^\circ$, 24350 reflections collected, 8948 unique ($R_{\text{int}} = 0.0779$). Final $GooF = 1.028$, $R1 = 0.0579$, $wR2 = 0.1381$, $R$ indices based on 6036 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 513 parameters, 30 restraints, $\mu = 2.047$ mm$^{-1}$. Hydrogen atoms of the carbamoyl group of ccnm were placed in idealised positions and refined using a riding model to the atom to which they are attached. Hydrogen atoms of the aqua ligands could not be accurately located from the Fourier difference map. Hydrogen atoms of the perchlorate anions were restrained using the SADI command. The bond length between H(5O) and O(5) restrained using DFIX command. Thermal parameters of O(20) and O(23) lattice parameters restrained using ISOR command.

Acknowledgements.

We thank the Australian Research Council for funding and for a postdoctoral fellowship (D. R. T.). A. S. R. C. acknowledges the award of an Australian Postgraduate Award scholarship.

Received: December 31, 2009.

Synthesis and Photophysical Properties of LaOF:Eu$^{3+}$ Nanocrystals

Tomasz Grzyb, Mariusz Weclawiak, and Stefan Lis*

Adam Mickiewicz University, Department of Rare Earths, Grunwaldzka 6, 60-780 Poznan, Poland
E-mail: blis@amu.edu.pl

Abstract. We report results concerning a new method of synthesis and photophysical properties of lanthanum oxyfluoride nanoparticles doped by Eu$^{3+}$ ions. Molten stearic acid has been used as environment for nanocrystal growth which allows for control of the particles size. Obtained precursor, annealed at temperatures 600 and 700°C, decomposed forming tetragonal or rhombohedral lanthanum oxyfluoride nanocrystals. Eu$^{3+}$ ions doped at concentration of 5%, have been used as a luminescence activator, which easily replace the Ln$^{3+}$ ions forming a host lattice. The prepared nanopowders showed an intensive red luminescence resulting from a charge transfer in the UV range.

Keywords: Lanthanum oxyfluoride; nanomaterials; luminescence

Introduction

Nanomaterials doped with lanthanides ions, Ln$^{3+}$, are being increasingly investigated due to their unique electrical, optical and electrochemical properties. The lanthanide ions doped nanomaterials with various inorganic hosts have made them applied in many fields, including displays like plasma display devices (PDP), field emission displays (FED), cathode ray tubes (CRT) and electroluminescent displays (EL),$^{1,2,3,4}$ optical telecommunication,$^{5}$ lasers,$^{6}$ biosensing and medical diagnostic.$^{7}$ Luminescence properties of the nanomaterials depend on the size of particles forming nanomaterials. In small crystals penetration of the UV light is more efficient and as a consequence more Ln$^{3+}$ could be excited. Moreover, it is known that the lifetime of the luminescence is connected with the particle size. According to host materials, it has been reported that nanoparticles could have significant extent of surface Ln$^{3+}$ ions due to a large difference in ionic radii between the doped Ln$^{3+}$ ion and ions forming the host lattice.$^{8}$

The luminescent properties of Ln$^{3+}$ ions originate from the transitions within the 4f shell. Characteristic for each Ln$^{3+}$ ion emission bands are narrow and can be more efficient due to an energy transfer from the inorganic matrix to the metal ion.

Rare earth oxyfluorides have been identified as one of the best host materials for Eu$^{3+}$ and Tb$^{3+}$ activators. Doped Ln$^{3+}$ ions can easily replace host cations to form a solid state solution. According to an earlier


© 2010 NWT-Verlag, Bornheim, Germany
study\textsuperscript{9} LnOF (Ln = La, Gd or Y) has two phases at room temperature. In rhombohedral LaOF, the space group is R-3m and La\textsuperscript{3+} is coordinated by four oxygen atoms and four fluorine anions with C\textsubscript{3v} site symmetry, as shown Fig. 1.\textsuperscript{10} In the tetragonal structure (Fig. 2), the La\textsuperscript{3+} ion is also eight coordinated to four oxygens and four fluorines but now the site symmetry of La\textsuperscript{3+} is a C\textsubscript{4v}. The tetragonal phase exhibits the space group P4/\textit{nm}m symmetry.\textsuperscript{11} Tetragonal LnOF are nonstoichiometric compounds due to easy substitution of the oxide ion by the fluoride ion, caused by their similar size, e.g. lanthanum oxyfluoride has the composition LaO\textsubscript{0.65}F\textsubscript{1.7}.

Most of the studies on lanthanide oxyfluorides LnOF have been done on their bulk crystals. There are few reports about LnOF nanocrystals and their photophysical properties.\textsuperscript{13,14,15} Methods used for LnOF preparation are based on high temperature solid state reactions between oxide Ln\textsubscript{2}O\textsubscript{3} and fluoride LnF\textsubscript{3}\textsuperscript{16} or between oxide and ammonium fluoride NH\textsubscript{4}F.\textsuperscript{11,12,17,18} For preparation of the nanocrystalline LnOF, decomposition of single-source precursors, like lanthanide trifluoroacetate, in oleic acid (with addition of the oleylamine and 1-octadecene) has been used.\textsuperscript{14,15}

### Results and discussion

XRD patterns of products obtained at different temperatures are presented in Figs. 3 and 4. The significant broadening of the reflections indicates the formation of nanocrystals. According to the JCPDS (Joint Committee on Powder Diffraction Standards) database nanocrystals prepared at 600\textdegree C have the tetragonal structure, and peaks for a temperature of 700\textdegree C are characteristic for rhombohedral LaOF.

XRD patterns were used for calculations of the crystallite size. The average crystallite sizes were estimated from the full-width at half-maximum (FWHM) of the diffraction peaks by the Scherrer equation $D = \frac{0.9 \lambda}{\beta \cos \theta}$, where D is the average grain size, the factor 0.9 is characteristic for spherical objects, $\lambda$ is the X-ray wavelength, $\theta$ and $\beta$ are the diffraction angle and full-width at half-maximum of an observed peak.\textsuperscript{19} Nanocrystals obtained at 600\textdegree C had an average size about 40 ± 5 nm and those obtained at 700\textdegree C had slightly larger size 48 ± 5 nm.

The TEM image of the sample is shown in Fig. 5; it indicates the aggregation of the nanoparticles. The observed sizes of the crystallites are comparable with those calculated from the XRD pattern.

\textsuperscript{9} W. H. Zachariasen, Acta Cryst. 1951, 4, 231.
\textsuperscript{12} J. Hölsä, E. Kestilä, J. Alloys Comp. 1995, 225, 89-94.
\textsuperscript{13} J. Lee, Q. Zhang, F. Saito, J. Alloys Comp. 2003, 348, 214-129.
\textsuperscript{17} E. Antic-Fidancev, J. Hölsä, J.-C. Krupa, M. Lastusaari, J. Alloys Comp. 2004, 380, 303-309.
\textsuperscript{19} P. Scherrer, Göttinger Nachrichten, 1918.
Figure 3. XRD pattern of tetragonal LaOF:Eu$^{3+}$ annealed at 600°C for 2h. 

Figure 4. XRD pattern of rhombohedral LaOF:Eu$^{3+}$ annealed at 700°C for 2h. 

Figure 5. TEM image of LaOF:Eu$^{3+}$ nanocrystals annealed at 700°C. 

The obtained products were characterized using luminescence spectroscopy. Excitation spectra both of lanthanide oxyfluorides (Figs. 6 and 7) show an intensive and broad band with the maximum at 277 nm. This broad excitation band is attributed to the $\text{O}_2^-$-Eu$^{3+}$ charge transfer (CT). 

Figure 6. Excitation spectrum of LaOF:Eu$^{3+}$ nanocrystals annealed at 600°C with observed emission at $\lambda = 612$ nm. 

Figure 7. Excitation spectrum of LaOF:Eu$^{3+}$ nanocrystals annealed at 700°C with observed emission at $\lambda = 612$ nm.
LaOF:Eu$^{3+}$ nanocrystals show intensive red luminescence originated from doped Eu$^{3+}$ ions. Figs. 8 and 9 show emission spectra of LaOF:Eu$^{3+}$ nanocrystals characteristic for the Eu$^{3+}$ ion transitions. It is well known that the Eu$^{3+}$ ion is a sensitive structure probe indicating the lattice symmetry of a host material. In the presented spectra, structural changes between samples heated at 600°C and 700°C influence the spectroscopy of Eu$^{3+}$. The transitions in the Eu$^{3+}$ ion environment change the crystal field influence on f-f transitions, which is mostly visible in the shift on the $^5D_0$-$^7F_2$ transition band and in the intensity of the $^5D_0$-$^7F_1$ transition band. Also the intensity of the luminescence is higher in the sample heated at 600°C.

Changes in the character of the luminescence spectra confirm the structural differences of the Eu$^{3+}$ ion environment as prepared for the two temperatures studied.

![Figure 8](image1.png)  
**Figure 8.** Emission spectrum of LaOF:Eu$^{3+}$ nanocrystals annealed at 600°C with excitation at $\lambda = 277$ nm.

![Figure 9](image2.png)  
**Figure 9.** Emission spectrum of LaOF:Eu$^{3+}$ nanocrystals annealed at 700°C with excitation at $\lambda = 277$ nm.

**Conclusions**

Lanthanum LaOF:Eu$^{3+}$ oxyfluoride nanocrystals were obtained by precipitation of the fluorides in molten stearic acid. The prepared precursors were calcined at two temperatures in order to find the best conditions for the study of luminescence properties and structure of the compounds. X-ray diffraction and transmission electron microscopy were applied to analyze the obtained products. Photoluminescent properties of the prepared nanopowders doped with Eu$^{3+}$ ions (concentration ~5 % mol) were investigated by analyzing their luminescence (excitation and emission) spectra, measured at room temperature. The luminescence properties, characteristic for Eu$^{3+}$ ions, and structural properties observed for the obtained materials strongly depend on the host and calcination temperature used. Those methods allow obtaining the product at quite low temperatures. Also, luminescence and structural properties of the materials obtained in this way are satisfactory.

**Experimental Section**

Eu(NO$_3$)$_3$ and La(NO$_3$)$_3$ solutions were prepared by dissolving appropriate oxides (99.99% Aldrich) in nitric acid, HNO$_3$. Stearic acid was introduced in a round-bottomed flask and heated to 80°C (stearic acid melts at 70°C). Appropriate amounts of Ln$^{3+}$ solutions were added to molten stearic acid and the flask was heated until water from added solutions was evaporated. In a second flask, stearic acid and ammonium fluoride, with 25% excess, were mixed and the mixture was heated. To begin the reaction, the solution from the second flask was slowly added to the first flask under vigorous stirring and the whole mixture was heated at 350°C for 1 h. The obtained precursor was annealed at temperatures of 600 and 700°C for 2 h.

XRD patterns were recorded with a Bruker AXS D8 Advance diffractometer using Cu Kα radiation ($\lambda = 1.541874$ Å) in the 2θ range from 20° to 60°. The TEM images were measured on a JEM 1200 EXII, JOEL transmission electron microscope, using an accelerating voltage of 75 kV.

© 2010 NWT-Verlag, Bornheim, Germany
The excitation and emission spectra were measured on a Hitachi F-7000 spectrofluorimeter at room temperature.

Acknowledgements

This work has been supported by the Polish Ministry of Science and Higher Education; Grant N N204 329736.

Received: December 31, 2009.
Chemiluminescence and Electrochemiluminescence of Lanthanide(III)/fluoroquinolone Systems

S. Lis*, M. Kaczmarek, K. Staninski, D. Komar, M. Buczkowska

Abstract. The use of chemiluminescence, CL, and electrochemiluminescence, ECL, methods in studies of fluoroquinolones, FQ, such as ciprofloxacin, norfloxacin and ofloxacin is presented. The CL studies of fluoroquinolones were carried out with the use of the following reaction systems in acidic solution: KBrO$_4$ - FQ; KNO$_3$ - H$_2$O$_2$ - FQ; Fe(II)/(III) - H$_2$O$_2$ - FQ, in the absence and presence of Tb(III) ions. In the ECL method the reagents were electrochemically generated on the Al/Al$_2$O$_3$ cathode. As the coreactants the aqueous solutions of K$_2$SO$_4$, K$_2$SO$_4$ and H$_2$O$_2$ were used. The systems of: KNO$_3$-H$_2$O$_2$-H$_2$SO$_4$ and Fe(II)/(III)-H$_2$O$_2$ (Fenton system) are the source of reactive forms of oxygen, such as peroxynitrous acid, hydroxyl radicals and singlet oxygen. Introduction of Tb(III) ions into the systems: KBrO$_4$-H$_2$SO$_4$-FQ and Fe(II)/(III) - H$_2$O$_2$ - H$_2$SO$_4$ – FQ caused a strong increase in the chemiluminescence intensity. The ECL observed in FQ solutions in the presence of Tb(III) ions has shown significant influence of coreactant on the emission intensity. In the system containing hydrogen peroxide the observed ECL intensity was 1,5 order of magnitude higher than that with other coreactants studied. The results of spectral analysis from CL and ECL have shown that main emitters in the reaction mixtures are the Tb(III) ions, with the emission maximum at ~ 545 nm, corresponding to the $^{5}D_{4}$ $\rightarrow$ $^{7}F_{5}$ transition. The excitation of Tb(III) in the analysed reaction systems: KBrO$_4$ - H$_2$SO$_4$ - FQ - Tb(III); KNO$_3$ - H$_2$O$_2$ - H$_2$SO$_4$ - FQ - Tb(III) and Fe(II)/(III) - H$_2$O$_2$ - H$_2$SO$_4$ - FQ - Tb(III) as well as in the ECL systems, is a result of energy transfer from the oxidation products of FQ to the uncomplexed Tb(III) ions.

Keywords: Lanthanides; Fluoroquinolones, Spectroscopy; Chemiluminescence; Energy transfer

Introduction

The quinolones are a family of synthetic broad-spectrum antibiotics. The majority of quinolones in medical use belong to the subset of fluoroquinolones, which have a fluorine atom attached the central ring system, typically at the 6-position. The fluoroquinolones (FQ) are synthetic chemotherapeutic agents used to treat bacterial infections. Complex formation of FQ with d- and f-electron metal ions is strongly dependent on pH solution. In the case of the lanthanides optimal conditions for the complex formation were found to be in the pH range 5.3 – 8.5, therefore in solutions of lower pH the complexation is less effective.

Chemiluminescence emission can be generated in many systems comprising oxygen or oxygen-containing compounds as oxidisers. As oxidizing agents have been used compounds containing oxygen in their structures, such as KBrO$_4$, or reaction systems generating reactive oxygen species (ROS): Fe(II)/(III)- H$_2$O$_2$ - the Fenton system, which is one of the main sources of reactive oxygen species such as hydroxyl radicals, OH, and singlet oxygen ($^{1}$O$_2$) or KNO$_3$ – H$_2$O$_2$ (forming peroxynitrous acid). These systems we have used for the CL

studies of the following fluoroquinolones: ciprofloxacin (CF), norfloxacin (NF) and ofloxacin (OF), as shown in chart 1, in the absence and presence of the Tb(III) ions in acidic conditions (pH ~1).

Chart 1. The structure of the fluoroquinolines studied: ofloxacin (OF), norfloxacin (NF) and ciprofloxacin (CF)

Chemiluminescence studies

The chemiluminescence was generated in the Fenton and KNO$_2$ - H$_2$O$_2$ systems. It was characterized by a very low intensity with a short duration. The presence of fluoroquinolones in these systems resulted in an increase in the CL intensity, while in the case of KBrO$_3$ - H$_2$SO$_4$ - FQ the CL emission was not measurable. Exemplary kinetic curves of CL decays in the systems with CF are presented in Fig. 1.

Figure 1. The kinetic curves of CL decay of the systems: Fe(II)/(III) - H$_2$O$_2$ - H$_2$SO$_4$ (1); KNO$_2$ - H$_2$O$_2$ - H$_2$SO$_4$ (2); KNO$_2$ - H$_2$O$_2$ - H$_2$SO$_4$ - CF (3); Fe(II)/(III) - H$_2$O$_2$ - H$_2$SO$_4$ - CF (4); Fe(II)/(III) - H$_2$O$_2$ - H$_2$SO$_4$ - CF - Tb(III) (5); KNO$_2$ - H$_2$O$_2$ - H$_2$SO$_4$ - CF - Tb(III) (6); KBrO$_3$ - H$_2$SO$_4$ - CF - Tb(III) (7). The concentration of Tb(III) = 1x10$^{-3}$ mol·l$^{-1}$; the initial concentration of H$_2$O$_2$ = 3x10$^{-2}$ mol·l$^{-1}$; Fe(II) = 1x10$^{-3}$ mol·l$^{-1}$; KBrO$_3$ = 8x10$^{-2}$ mol·l$^{-1}$; KNO$_2$ = 6x10$^{-2}$ mol·l$^{-1}$; CF = 6x10$^{-7}$ mol·l$^{-1}$ and only in the system KBrO$_3$ - H$_2$SO$_4$ - CF - Tb(III) the initial concentration of CF was 2x10$^{-5}$ mol·l$^{-1}$; pH ~1.

The most intensive CL was measured in the system Fe(II)/(III) - H$_2$O$_2$ - H$_2$SO$_4$ - FQ. Spectral analysis of the chemiluminescence from the systems was performed using the method of cut-off filters as we described earlier. Spectral analysis of the chemiluminescence from the systems was performed using the method of cut-off filters as we described earlier. Fig. 2 shows exemplary CL spectra (as normalized spectral distributions of CL) of the reaction systems KNO$_2$ - H$_2$O$_2$ - H$_2$SO$_4$ - CF and Fe(II)/(III) - H$_2$O$_2$ - H$_2$SO$_4$ - CF. The spectrum of KNO$_2$ - H$_2$O$_2$ - H$_2$SO$_4$ - CF shows a broad emission band with a maximum at $\lambda \sim 510$ nm, which is similar to the spectrum obtained by Francis and Adcock. However for the reaction system Fe(II)/(III) - H$_2$O$_2$ - H$_2$SO$_4$ - CF the CL spectrum

9 K. Staninski, M. Kaczmarek, S. Lis, D. Komar, A. Szyczewski, J. Rare Earths 2008, 26, 131-137.
reveals two bands with maxima at \( \lambda \sim 440 \text{ nm} \) and \( \lambda \sim 515 \text{ nm} \). Identical spectra were obtained for the systems with NF. In the case of OF the CL spectral distributions of the mixtures KNO\(_2\) - H\(_2\)O\(_2\) - H\(_2\)SO\(_4\) - OF and Fe(II)/(III) - H\(_2\)O\(_2\) - H\(_2\)SO\(_4\) - OF are similar and show the emission band at \( \lambda \sim 515 \text{ nm} \). The obtained spectral distributions of CL for the systems KNO\(_2\) - H\(_2\)O\(_2\) - H\(_2\)SO\(_4\) - CF or NF and Fe(II)/(III) - H\(_2\)O\(_2\) - H\(_2\)SO\(_4\) - CF or NF are different from the fluorescence spectra of CF or NF recorded in the solution of H\(_2\)SO\(_4\), which proves that excited products of oxidation of the fluoroquinolones are emitters in these systems. Only the distribution for the CL from the reaction with ofloxacin (\( \lambda_{\text{max}} \sim 515 \text{ nm} \)) was comparable to its fluorescence spectrum in 0.1M sulfuric acid (\( \lambda_{\text{max}} \sim 508 \text{ nm} \)). Interactions of fluoroquinolones with the ROS are not ambiguously described in the literature. The defluorination process of FQs, typical for neutral aqueous solution, does not occur under acidic conditions neither with FQs bearing electron donating groups. Under such conditions inefficient degradation of the alkylamino side chain occurs and leaves the heterocyclic fluorine intact. However, NF and CF, which defluorinate in neutral solution, undergo in acidic solution stepwise degradation of the piperazine side-chain until this latter is reduced to an amino group. The mechanism of this class of reactions has not been clarified yet.\(^1\)

---

Optimization of experimental parameters, such as concentrations of the components, pH range, etc., will be the subject of further studies.

Figure 3. The normalized spectral distribution of CL of the systems: Fe(II)/(III) - H_2SO_4 - FQ - Tb(III) (1) and KBrO_3 - H_2SO_4 - CF - Tb(III) (2). The initial concentration of H_2O_2 = 3x10^{-2} mol·l^{-1}, KBrO_3 = 8x10^{-2} mol·l^{-1}, CF = 4x10^{-6} mol·l^{-1}, Tb(III) = 1x10^{-3} mol·l^{-1}, and Fe(II) = 1x10^{-3} mol·l^{-1}; pH ~1.

Electrochemiluminescence studies

Electrochemiluminescence, ECL, in aqueous solutions utilizing aluminium cathodes usually makes use of the peroxodisulfate ion, S_2O_8^{2-}, which assists in the formation of active radicals on the electrode surface.\textsuperscript{12,13} Electrochemical excitation of an organic compound (A) or its metal complex depends on its red-ox properties or experimental conditions and proceeds according to the reactions:

\[ A + e^- \rightarrow A^* , \]
\[ S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{*} \]
\[ A^* + SO_4^{*} \rightarrow A + SO_4^{2-} \]
\[ A^* \rightarrow A + hv \]

If energy levels of the lowest lying empty orbital of the oxidized form of the organic molecule and the level of the reducer are appropriately matching, the electron can be introduced onto the lowest orbital (LUMO), which causes a formation of the product in the excited state. The use of peroxodisulfates as a coreactant in the ECL process in aqueous solution is favourable, since they show a low reactivity in relation to water (k(SO_4^{2-} + H_2O) < 60 l·mol^{-1}·s^{-1}). Unfortunately, there is a side effect of the use of S_2O_8^{2-}, related with its participation in oxidation processes of F-centers of the Al_2O_3 nanolayer covering the cathode. A radical decay under influence of hydrated (hot) electrons causes filling up the 1P excited state in the F-center of Al_2O_3, radiationless deactivation of the 3P state, and next transition to the 1S ground state:\textsuperscript{14}

\[ e^- \rightarrow e_{aq}^- \]
\[ e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{*} \quad (k = 1.2 \cdot 10^{10} l·mol^{-1}·s^{-1}) \]
\[ F^* (1P) \rightarrow F^* (3P) \]
\[ SO_4^{*} + F \rightarrow F^* + SO_4^{2-} \]

In aqueous solution, containing $\text{S}_2\text{O}_8^{2-}$, a weak emission appearing with a maximum centered at ~420 nm interferes in the spectral analysis of the systems showing a low ECL yield such as fluoroquinolones, in this spectral range. Our studies were carried out with the use of various coreactants, such as peroxodisulfates, oxalates and $\text{H}_2\text{O}_2$. The results show that the most intense ECL emission was observed in the systems containing $\text{H}_2\text{O}_2$, while the weakest ECL intensity appeared in the case of the oxalate system. The ECL spectra registered in the aqueous solution of FQs are shown in Fig. 4. The ECL bands recorded in the studied system are similar to that obtained in the photoexcitation process. Studies of ECL using Tb(III) were carried out in solutions containing hydrogen peroxide as the coreactant. The characteristic emission for the employed Tb(III) ions was observed in the case of $\text{H}_2\text{O}_2$ is shown in Fig. 5. The most intense ECL emission, characteristic for Tb(III) ions was observed in the case of ciprofloxacin in acidic solution. The mechanism of the energy transfer to the Tb(III), similarly as in the case of the CL system, is a result of the oxidation of fluoroquinolone and generation of transitional products (probably in the peroxide form), which decay provides a sufficient energy to the Tb(III) excitation.

![ECL spectra of FQs in aqueous solution](image1)

**Figure 4.** ECL spectra of FQs in aqueous solution, experimental conditions: pH 3.5; concentration of FQ $= 10^{-4}$ mol·l$^{-1}$ in $\text{Na}_2\text{S}_2\text{O}_8$ solution of (0.1 mol·l$^{-1}$); cathode: Al/$\text{Al}_2\text{O}_3$; anode: Pt wire; pulses: amplitude 30V, frequency 30Hz, charge 90 $\mu$C/pulse.

![ECL spectra of FQ containing Tb(III) ions](image2)

**Figure 5.** ECL spectra of FQ containing Tb(III) ions ($10^{-3}$ mol·l$^{-1}$) and $\text{H}_2\text{O}_2$ ($10^{-3}$ mol·l$^{-1}$) in aqueous solution. Experimental conditions were the same as in Fig. 4.
The results of spectral analysis obtained from CL and ECL have shown that the main emitters in the systems studied are the Tb(III) ions, with the emission maximum at $\lambda \sim 545$ nm, corresponding to the $^5D_4 \rightarrow ^7F_5$ transition. The excitation of terbium(III) ions in the CL systems is a result of energy transfer from the oxidation products of fluoroquinolones to the Tb(III) ions.

**Experimental Section**

Ultraweak photon emissions (chemiluminescence) were measured with the use of the earlier described equipment.\(^{15}\)

Electrochemiluminescence was generated with electrically rectangular pulses on the aluminium electrode that was covered with a natural nanolayer oxide, and the ECL measurements were carried out using the experimental setup as we described earlier.\(^{13}\) Emission of “hot” electrons into the solutions was due to the use of large potential differences (> 40V) and a thin layer of oxide occurred.

Chemicals used in this study were ciprofloxacin, norfloxacin, ofloxacin, terbium(III) oxide, $\text{H}_2\text{SO}_4$, KNO$_2$, H$_2$O$_2$, KBrO$_3$, Na$_2$S$_2$O$_8$, Fe(NH$_4$)$_2$(SO$_4$)$_2$. All the reagents used were of purity not lower than analytical grade. All solutions were prepared with distilled water. Tb(III) chloride was obtained by dissolving Tb$_4$O$_7$ in hydrochloric acid.

All of the chemiluminescence studies were performed in the same way. The CL process was each time initiated by adding a solution of $\text{H}_2\text{O}_2$ or KBrO$_3$ to solutions containing the other components of the reaction mixture, of the total volume of 10 ml.

In the ECL study as the supporting electrolyte, a solution of Na$_2$S$_2$O$_8$ in redistilled water was used. In order to eliminate side radical reactions, no buffers were used, and the required pH value was obtained adjusted by the addition of NaOH or HCl.

**Acknowledgements**

This work has been supported by a grant of Polish Ministry of Science and Higher Education nr N N204 028236.

Received: December 31, 2009.

---

\(^{15}\) M. Kaczmarek, S. Lis, *J. Fluoresc.* 2006, 16, 825-830.
Self-Assembly of Polynuclear Arrays for Sensing Purposes

Josef Hamacek*

Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai E.-Ansermet, CH-1211 Geneva 4, Switzerland.
E-mail: Josef.Hamacek@unige.ch

Abstract. The research activities of Hamacek’s group at the Department of Inorganic, Analytical and Applied Chemistry of the University of Geneva are reviewed briefly. The contribution is focused on the present development of polynuclear lanthanide-containing systems for sensing purposes. The structural and physico-chemical properties of tri- and tetranuclear complexes with organic receptors are discussed.

Keywords: Lanthanides; Coordination; Self-Assembly; Polynuclear Complexes

Introduction

A number of present analytical and biomedical applications use lanthanide-containing complexes due to their interesting luminescent\(^1\) or paramagnetic\(^2\) properties. Between potential candidates for these purposes, only those with good thermodynamic and kinetic stability can be taken into consideration. In addition, the complexing ligand should possess convenient coupling groups for future labelling of biomolecules. The majority of systems is based on mononuclear highly stable complexes, i.e., complexes with ligands derived from polycarboxylic acids such as DOTA and DTPA. Despite a quite satisfactory performance of these compounds, there is still a potential for a significant response enhancement. For instance, one may resort to discrete polynuclear complexes, where the measured signal will correspond to the sum of contributions coming from all responding cations. This effect can be easily quantified like, for example, the density of relaxivity, which is used for comparing the efficiency of different paramagnetic compound.\(^3\)

In the past, the polynuclear complexes have been mainly studied with transition metals. Lanthanide-based systems are relatively less reported because of difficulties to satisfy their high coordination number. From the topological point of view, different spatial organisations of metallic cations in polynuclear assemblies may be distinguished. Therefore, one can speak about mono-, two- and three-dimensional arrays. Linear polynuclear arrays were mainly developed by Piguet \textit{et al}. in the form of helicates (the assemblies containing up to four lanthanides),\(^4\) but some other systems were investigated.\(^5\) The family of two-dimensional arrays mostly consists of complexes with triangular\(^6\) or tetragonal\(^7\) arrangement of metallic cations. However, much larger 2D

---

polynuclear compounds may be also generated. Except polynuclear clusters, discrete self-assembled three-dimensional lanthanide complexes are still scarcely found in the literature. In this context, let us give the examples of dendrimeric complexes, which are advantageously used for enhancement of both, luminescence and the water relaxivity.

Herein, we present the self-assembly of two polynuclear systems developed recently in our laboratory. Such nanometric complexes may be potentially used as luminescent markers, paramagnetic or multimodal probes. The X-ray crystal structures, the structure in solution and photophysical properties of these remarkable supramolecular compounds are discussed.

The two-dimensional complexes

In search for a suitable organic receptor for Ln(III), we have designed a small ligand L1 possessing two pyridinecarboxylates connected via the amide nitrogen (Figure 1). This structural motif leads to a highly conjugated electronic system, which would be suitable for sensitizing Ln(III) luminescence. We can distinguish two distinct coordination sites within L1: (i) the pentacoordinate cavity formed by two carbonylpyridines and the amide nitrogen, and (ii) the bidentate dicarbonyl site. In practice, Ln(III) complexes with L1 are obtained by the reaction of Ln(III) perchlorates with a dimethyl ester precursor and its simultaneous hydrolysis.

Figure 1. Chemical structures of the ligands.

The crystal structure of resulting complexes (Figure 2) shows the formation of trinuclear complexes [Eu$_3$L$_1$(H$_2$O)$_6$] with triangular topology of metallic cations. Indeed, Eu(III) cations are coordinated in the main pentacoordinate cavity. The deprotonation of the amide nitrogen and the terminal carboxylates compensates completely the positive charge of lanthanides. Such monometallic complexes are consequently interconnected by bidentate sites, whose two carbonyl oxygens are well predisposed for coordinating to the neighbouring cation. This peculiar coordination mode minimizes the potential energy of the system by maximizing the number of coordination bonds (principle of maximum site occupancy). Finally, the europium coordination sphere is completed up to nine with two water molecules. Despite this generally unfavourable fact, the complexes exhibit strong luminescence. The quantum yield measured in water ($\Phi \sim 13\%$) is almost three times lower than the value

---

in DMSO, but it remains satisfactory for potential applications. The overall emission spectra are similar in both solvents and show the maximum at 617 nm (Figure 2).

The presence of two water molecules per metallic cation, confirmed by photophysical studies, is promising for the potential use as a contrast agent for magnetic resonance imaging (MRI). Nevertheless, the investigation of the relaxivity of analogous Gd(III) complexes is still under progress.

**Figure 2.** A view down of the triangular structure of \([\text{Eu}_3\text{L}_1(\text{H}_2\text{O})_6]\) and the related emission spectra.

The three-dimensional complexes

The formation of three-dimensional complexes is achieved with a tripodal ligand \(\text{L}_2\). Although \(\text{L}_2\) is potentially ninecoordinate, the short spacer induces sterical constraints and the ligand adopts an opened conformation ("trefoil leave"). In term of thermodynamics, the effective concentration toward the formation of monometallic complexes with \(\text{L}_2\) is too low.\(^{14}\) However, the opened conformation leads to the self-assembly of more complicated compounds, i.e., tetrametallic complexes \([\text{Ln}_4\text{L}_2]^{12+}\). The crystal structure of the terbium analogue shows in details that each strand of \(\text{L}_2\) is coordinated to a different cation (Figure 3). Therefore, each metal is coordinated by three different \(\text{L}_2\), which allows to completely satisfy its coordination number nine. The four metallic cations are thus localised in vertexes of a regular tetrahedron that represents the simplest three-dimensional arrangement of lanthanide cations.

**Figure 3.** Tetrahedral arrangement of Tb(III) cations in the crystal structure of \([\text{Tb}_4\text{L}_2]^{12+}\).

---


The tetrahedral structure of \([\text{Ln}_4\text{L}_2]^{12+}\) is maintained in acetonitrile solution. This high symmetry is confirmed by the NMR spectra of (i) isolated compounds (\(\text{Ln} = \text{Nd, Eu, Y, Yb, Lu}\)) as well as of (ii) acetonitrile solutions prepared by stoichiometric mixing of \(\text{L}_2\) with lanthanides. The observation of diastereotopic methylene protons is an unambiguous sign of the helical wrapping of strands about cations and these tetrahedral complexes may be reasonably considered as 3D helicates. ESMS analyses clearly show the series of tetrancular complexes differing in the number of associated perchlorate counteranions (Figure 4). Qualitative information about the coordination sphere is brought by photophysical studies. The long luminescence lifetime of \([\text{Eu}_4\text{L}_2]^{12+}\) in acetonitrile (\(\tau = 1.85(3)\) ms) indicates the absence of coordinating solvent molecules and the quantum yield is typical for pyridinedicarboxamide ninecoordinated Eu(III) complexes.\(^{15}\)

Except the tetrametallic tetrahedral complex, additional polymetallic species were identified for other stoichiometric ratios \([\text{Ln}]/[\text{L}_2]\). The whole speciation of the system \(\text{Ln(III)}-\text{L}_2\) is currently studied by spectrophotometry.

**Figure 4.** (a) ESMS spectrum of \([\text{Eu}_4\text{L}_2]\)(\(\text{ClO}_4\))\(_6\) in acetonitrile. (b) Emission spectra of tetrahedral complexes in the solid state.

**Conclusions**

The polynuclear complexes with \(\text{L}_1\) and \(\text{L}_2\) exhibit high molecular symmetries with a relative proximity of metallic cations (7.0 Å and 9.35 Å, respectively). The trigonal and tetrahedral structures of these assemblies are significantly influenced by the ligand design and preorganization for targeted complexes (spacer length, coordination units). Moreover, playing with the nature of coordination sites allows tuning the composition of the lanthanide coordination sphere. While its complete saturation by organic ligands (\(\text{L}_2\)) is rather predetermined for preparing luminescent probes, the unsaturated sphere is required for MRI agents (\(\text{L}_1\)). However, in the case of the homometallic Eu(III) complex with \(\text{L}_1\), the exceptional luminescence is observed despite two coordinated water molecules.

In perspective, heterometallic compounds will be prepared by incorporating of both, paramagnetic (i.e., Gd) and light-emitting (i.e., in visible - Eu, Tb; in near IR – Nd, Yb) lanthanides, into the same molecule. Although this is a challenging task, we believe that our polynuclear systems represent promising precursors for functional multimodal probes.

Experimental Section

Synthesis. Starting materials and solvents were purchased from commercial sources. Ligands L1 and L2 were synthetised according to previously published procedures.11,13 Lanthanide perchlorates were prepared from the corresponding oxides (Rhodia and Aldrich, 99.99%) and dried according to published procedures.16

Spectroscopic and analytical measurements. The crystallographic data were collected at 150 K on a Stoe IPDS diffractometer with graphite monochromated Mo-Kα radiation. The structures were solved by direct methods (SIR97),17 all other calculations were performed with XTAL program package.18 1H NMR spectra were recorded on a high-field NMR spectrometer (400 MHz; Bruker). ESMS spectra were measured on a Finnigan SSQ7000 instrument. Luminescence spectra and decays in solution were recorded on a Perkin-Elmer LS-50 spectrometer.

Acknowledgements.

This work has been supported by the University of Geneva, the Swiss National Science Foundation, and the COST D38 Action.

Received: December 31, 2009.

Biocompatibility of Eu\textsuperscript{3+}-doped Gadolinium Hydroxide and Oxide Nanorods

Yvonne Kohl,\textsuperscript{[a]} Eva Hemmer,\textsuperscript{[b]} Kohei Soga,\textsuperscript{[b]} Sanjay Mathur,\textsuperscript{[c]}* and Hagen Thielecke\textsuperscript{[a]}

\textsuperscript{[a]} Fraunhofer Institute for Biomedical Engineering, Department of Biohybrid Systems, Ensheimer Straße 48, 66386 Sankt Ingbert, Germany
\textsuperscript{[b]} Tokyo University of Science, Department of Materials Science and Technology, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
\textsuperscript{[c]} University of Cologne, Institute of Inorganic Chemistry, Greinstraße 6, 50939 Cologne, Germany
E-mail: sanjay.mathur@uni-koeln.de

Abstract. Nanostructures with optical and magnetic properties are promising candidates for biomedical applications, e.g. as diagnostic agents, biosensors, coatings on implants or as drug delivery systems. In particular, Ln\textsuperscript{3+} containing nanostructures are gaining interest due to their outstanding optical properties, which may overcome the problems of recently used organic dyes (photo-bleaching, scattering). Due to their magnetic properties, magneto-optical Ln\textsuperscript{3+}-based nanostructures represent a new material class for bioimaging. With regard to potential applications as contrast agents in MRI, Gd\textsuperscript{3+}-containing compounds are suitable due their high magnetic moment. Lanthanide ions, such as europium (Eu\textsuperscript{3+}) show intensive luminescence under UV excitation. The combination of the magnetic and optical properties of the lanthanides represents a new class of biomarkers, which gives more detailed information than one single (optical or magnetic) imaging method. In this study Eu\textsuperscript{3+} doped Gd(OH)\textsubscript{3} and Gd\textsubscript{2}O\textsubscript{3} nanorods were synthesized by solvothermal decomposition of a gadolinium-based metal-organic precursor. Using human lung epithelial cells the cytotoxicity as well as internalization of the obtained Eu\textsuperscript{3+} doped nanorods were investigated with regard to potential applications as a biomarkers.

Keywords: Gadolinium hydroxide, Gadolinium oxide, Europium-doped, Nanorods, Solvothermal synthesis, Cytotoxicity

Introduction

The possibilities of using nanostructured materials in medicine have been widely explored due to intrinsic properties\textsuperscript{1} of these materials, which qualify them as candidates for drug delivery systems.\textsuperscript{2-9} Recent studies have shown the ability of engineered nanostructures to overcome biological barriers, which have triggered their applications in drug delivery and controlled release, as active surfaces in implants and as biomarkers in cell tracking or diagnostic imaging.\textsuperscript{5678910} Due to their strong signal per molecular recognition site nanoparticles are

\textsuperscript{2} Z. Wang, W. K. Chui, P. C. Ho, Pharm. Res. 2009, 26, 1162.
\textsuperscript{6} D. B. Resnik, S. S. Tinkle, Nanomedicine 2007, 2, 345.
\textsuperscript{7} O. V. Sata, J. Nanobiotechnol. 2004, 6.
\textsuperscript{8} A. Doat, M. Fanjul, F. Pelle, E. Hollande, A. Lebugle, Biomaterials 2003, 24, 3365.
of great interest, especially as contrast agents for diagnostic molecular imaging. Current research approaches deal with extended use of particulate contrast agents for molecular diagnostics and therapeutic application. Particulate contrast agents are currently approved for ultrasound imaging (USI) as well as magnetic resonance imaging (MRI). Accredited particulate contrast agents are predicated on the paramagnetic characteristic of nanoparticles. Gadolinium-based contrast agents, such as Manevist® (Schering, Berlin, Germany) are used in medical diagnostics (MRI, URI). However, these compounds suffer from several disadvantages. In order to induce higher sensitivity, the synthesis of novel contrast agents with significantly higher relaxivities than conventional MRI agents is required. Besides MRI, diagnostic tools based on fluorescent markers are widely applied in medicine as well as for visualization, measurement and investigation of biological phenomena. Commonly, organic dyes have been used as biomarkers, but suffer from color fading resulting in a limited application time. In particular under excitation with ultraviolet light, scattering, auto-fluorescence and photo toxicity are further problems. In order to overcome these problems, quantum dots have been investigated as an alternative. Herein, the main disadvantage is their toxicity, which requires complex surface coatings or core-shell structures. Lanthanide-based inorganic materials with their outstanding optical and magnetic properties are interesting alternatives for applications such as biomarkers, sensors and contrast agents in biomedicine and may overcome the mentioned problems. For example, Eu³⁺ doped upconverting phosphors are promising candidates for applications in fluorescence biolabeling due to absorption of infrared radiation and emission in the visible spectrum. The combination of magnetic and optical properties is attracting increasing attention, and the synthesis of opto-magnetic nanoparticles for biolabeling applications consisting of a magnetic host material (Gd₂O₃, Fe₂O₃) doped with europium ions has been reported. In this context, gadolinium possesses unique magnetic properties, such as a high magnetic moment (7.94 μB). Due to this property gadolinium-containing nanoparticles are used for various applications in the medical field. For MRI an accurate diagnosis is obtained by using positive contrast agents such as ionic gadolinium based materials in order to enhance the image contrast in living tissue. Clinically available products are mostly low molecular weight Gd(III) chelates, including DTPA, Gd-DOTA and their derivates. However investigations of Gd₂O₃ have shown that gadolinium oxide is a promising candidate for MRI. Due to their strong luminescence europium (Eu³⁺) could be used in new nanoparticulate contrast agents for non-invasive diagnostic imaging techniques. In Eu³⁺ doped Gd₂O₃ the optical properties of gadolinium and the magnetic properties of europium are combined resulting in opto-magnetic devices, providing more detailed information than the use of conventional contrast agents, which are based on one single (magnetic or optical) method.

The approach of this study involves the preparation of europium-doped gadolinium hydroxide (Gd(OH)₃:Eu³⁺) and gadolinium oxide (Gd₂O₃:Eu³⁺) with regard to applications as biomarkers. The cytotoxicity of recently in medicine applied nanoparticles, e. g. iron oxide as MRI contrast agent and carrier systems in cancer therapies, is still not completely clarified. Therefore an intensive and careful investigation of nanoparticulate biomarkers

is required. Under these aspects, we investigated the biocompatibility of Eu$^{3+}$-doped Gd(OH)$_3$ and Gd$_2$O$_3$ nanostructures with respect to potential in vivo applications.

**Preparation and characterisation of Eu$^{3+}$-doped Gd(OH)$_3$ and Gd$_2$O$_3$ nanostructures**

Gadolinium-containing nanostructures were synthesized by solvothermal decomposition of the gadolinium oleate complex. The X-ray diffraction pattern recorded on as-prepared Eu$^{3+}$-doped samples shows the characteristic reflections for crystalline Gd(OH)$_3$, whereas the doping process does not take influence on phase purity or crystallinity when compared to undoped Gd(OH)$_3$ nanostructures$^{31}$ (Figure 1a). Post-thermal treatment of Eu$^{3+}$-Gd(OH)$_3$ at 600 °C for 2 h led to dehydration of the hydroxide phase to gadolinium oxide, Gd$_2$O$_3$ (Figure 1b).

![Figure 1. X-ray diffraction patterns of Eu$^{3+}$-doped as-prepared (a) and post-annealed (b) samples.](image)

Figure 1. X-ray diffraction patterns of Eu$^{3+}$-doped as-prepared (a) and post-annealed (b) samples.

The as-prepared Gd(OH)$_3$ powders consist of elongated structures with homogeneous lengths of several hundred nanometers and diameters of approximately 30 nm as observed in SEM (Figure 2a). Due to the ratio of length and diameter (aspect ratio: 15-20) the obtained nanostructures can be classified as nanorods. Doping with europium ions results in an inhomogeneous morphology of Gd(OH)$_3$:Eu$^{3+}$ (Figure 2b). Besides nanorods of more than 100 nm in length agglomerations of irregular shaped particles are observed. Similar morphologies are observed after post-thermal treatment resulting in Gd$_2$O$_3$:Eu$^{3+}$ (Figure 2c).

![Figure 2. (a) TEM image of as-prepared Gd(OH)$_3$ nanorods obtained by solvothermal decomposition of Gd(oleate)$_3$. FE-SEM image of (b) Eu$^{3+}$-doped Gd(OH)$_3$ and (c) post-annealed ($\Delta T = 600$ °C) Eu$^{3+}$-doped Gd$_2$O$_3$ samples.](image)

Figure 2. (a) TEM image of as-prepared Gd(OH)$_3$, nanorods obtained by solvothermal decomposition of Gd(oleate)$_3$. FE-SEM image of (b) Eu$^{3+}$-doped Gd(OH)$_3$ and (c) post-annealed ($\Delta T = 600$ °C) Eu$^{3+}$-doped Gd$_2$O$_3$ samples.

Formation of gadolinium hydroxide was also confirmed by FT-IR spectroscopy (Figure 3a). A strong peak and band in the range from 3600 to 3100 cm$^{-1}$ can be related to vibration of hydroxyl groups. Further peaks in the range from 1650 to 1510 cm$^{-1}$ can be assigned to metal carboxylate vibration which may be due to residual oleate groups originating from Gd(oleate)$_3$ precursor. FT-IR spectra recorded on post-annealed powders are

---

shown in Figure 3b. With increasing annealing temperature the water and carboxylate groups are removed from the powders and no bands due to water or carboxylate groups are observed after calcination at 1100 °C. The peak observed at 540 cm\(^{-1}\) can be assigned to M-O-vibration indicating the formation of gadolinium oxide phase.

Figure 3. FT-IR spectra of Eu\(^{3+}\)-doped as-prepared (a) and post-annealed (b) samples.

Luminescence properties of the obtained Eu\(^{3+}\)-doped powders were investigated by photoluminescence spectroscopy. The recorded excitation and emission spectra of annealed powders are shown in Figure 4a.

Figure 4. (a) Excitation (\(\Delta T=600 {^\circ\text{C}}\)) and emission (\(\Delta T=1100 {^\circ\text{C}}\)) spectra of Gd\(_2\)O\(_3\):Eu\(^{3+}\). (b) Energy level diagram of Eu\(^{3+}\).

Both spectra show the characteristic peaks corresponding to Eu\(^{3+}\) f-f transitions (Figure 4b). The excitation spectrum of Eu\(^{3+}\):Gd\(_2\)O\(_3\) powders annealed at 600 °C shows three intensive absorption peaks at 393, 465 and 532 nm at a monitoring wavelength of 612 nm, which are referred to \(^7F_0 \rightarrow ^5L_6\) (393 nm), \(^7F_0 \rightarrow ^5D_2\) (465 nm) and \(^7F_{0,1} \rightarrow ^5D_1\) (532 nm) transitions. The emission spectrum of Gd\(_2\)O\(_3\):Eu\(^{3+}\) annealed at 1000 °C shows a maximum peak in the red range of the visible spectrum at 610 nm, which is due to the \(^5D_0 \rightarrow ^7F_2\) transition. Further peaks are observed at 578, 590, 626, 648 and 704 nm, which are assigned to \(^5D_0 \rightarrow ^7F_J\) (\(J = 0, 1, 2, 3, 4\)) transitions. Figure 5 represents a section of the emission spectra of as-prepared and post-annealed powders showing characteristic peaks for electric (\(I_{ED}\)) and magnetic (\(I_{MD}\)) dipole emission. The ratio between the intensity of electric dipole emission and the intensity of magnetic dipole emission, \(I_{ED} / I_{MD} = R(D_0 \rightarrow F_2) / R(D_0 \rightarrow F_1)\), increases with increasing annealing temperature. While the \(I_{MD}\) is almost unaffected by changes of the host, the

$I_{\text{ED}}$ is strongly affected by the surrounding of the Eu$^{3+}$ ion. An increase of the covalency with the charge of the ligands gives a stronger crystal field resulting in increased $I_{\text{ED}}$. Therefore, the observation of the emission spectra can be attributed to the change from monovalent OH$^-$ to divalent O$^{2-}$ in the environment of luminescent Eu$^{3+}$ centres when hydroxide is transformed into oxide resulting in changes in the crystal field. Herein, an intermediate state between the pure hydroxide (as-prepared sample) and oxide (sample annealed at 1100 °C) phase is represented by powders obtained at 600 °C.

**Cytotoxicity of Eu$^{3+}$-doped Gd(OH)$_3$ and Gd$_2$O$_3$ nanostructures**

With respect to potential *in vivo* applications in biomedicine, the biocompatibility of the synthesized Gd(OH)$_3$:Eu$^{3+}$ and Gd$_2$O$_3$:Eu$^{3+}$ nanostructures was investigated. The metabolic activity was determined using the WST-1 assay. This assay is based on the cleavage of stable non-fluorescent tetrazolium salt WST-1 by metabolically active cells to an orange formazan dye. Following two different times (4 h and 24 h) of continuous exposure to the nanoparticles, quantitative analysis of cell viability was carried out. Each experiment included the positive control TritonX-100 at 2% inducing membrane damages and therefore cell death and nanoparticle-free cell culture medium as negative control. In case of Gd(OH)$_3$:Eu$^{3+}$ and Gd$_2$O$_3$:Eu$^{3+}$ no significant decrease of the mitochondrial activity was observed at a nanorod concentration of 50 µg/ml (Figure 6). Even a higher concentration of 250 µg/ml Gd(OH)$_3$:Eu$^{3+}$ and Gd$_2$O$_3$:Eu$^{3+}$ induced no significant decrease of the mitochondrial activity, when compared to the negative control (Figure 6).

**Figure 5.** Influence of the hydroxyl groups on the emission spectra of Gd$_2$O$_3$:Eu$^{3+}$ (■: electric dipole emission $I_{\text{ED}}$, ●: magnetic dipole emission, $I_{\text{MD}}$).

**Figure 6.** Effect of Eu$^{3+}$-doped gadolinium hydroxide and Eu$^{3+}$-doped gadolinium oxide nanostructures on the metabolic activity of A549 cells. Cells were treated with 50 µg/ml and 250 µg/ml of gadolinium-containing nanostructures. The effect on proliferation rate after 4 h (grey) and 24 h (black) of exposure was quantified by WST-1 assay. Data are expressed as mean ± SD (n = 3). Control cells without nanostructures treatment are 100%.
The effect of the nanostructures on cell proliferation was investigated by the BrdU assay. This colorimetric immunoassay is based on the measurement of BrdU (5-bromo-2'-deoxyuridine) incorporation during DNA synthesis. Using the BrdU assay the Gd(OH)$_3$:Eu$^{3+}$ and Gd$_2$O$_3$:Eu$^{3+}$ nanostructures showed no significant decrease of the proliferation rate of A549 cells after 4 and 24 h of exposure at concentrations up to 250 µg/ml (Figure 7).

**Figure 7.** Effect of Eu$^{3+}$ doped gadolinium hydroxide and Eu$^{3+}$ doped gadolinium oxide nanostructures on the proliferation rate of A549 cells. Cells were treated with 50 µg/ml and 250 µg/ml of gadolinium-containing nanostructures. The effect on proliferation rate after 4 h (gray) and 24 h (black) of exposure was quantified by BrdU assay. Data are expressed as mean ±SD (n = 3). Control cells without nanostructures treatment are 100%.

The membrane integrity of the A549 cells incubated with europium-doped nanostructures was measured by the LDH assay. This assay measures lactate dehydrogenase (LDH) released from damaged cells. Following the exposure of the prepared samples at highest dosage level (250 µg/ml), LDH release was not significantly higher than in case of the nanoparticle-free control (Figure 8). Further, no time-dependent effect on the plasma membrane at any of the tested concentrations could be observed.

**Figure 8.** Effect of Eu$^{3+}$ doped gadolinium hydroxide and Eu$^{3+}$ doped gadolinium oxide nanostructures on the membrane integrity of A549 cells. Cells were treated with 50 µg/ml and 250 µg/ml of gadolinium-containing nanostructures. The effect on proliferation rate after 4 h (gray) and 24 h (black) of exposure was quantified by LDH assay. Data are expressed as mean ±SD (n = 3). Control cells without nanostructures treatment are 100%.

Additionally to the cytotoxicity tests a living/dead staining was performed. All fluorescence images were taken after 24 h of exposure. The observed results correlate with the results obtained from cytotoxicity assays. The
incubation of cell culture medium without nanostructures shows a low percentage (3.21%) of dead A549 cells. 96.79% of A549 control cells are viable. After the exposure to 250 µg/ml Gd₂O₃:Eu³⁺ the amount of dead cells increased by 0.30% to 4.19% compared to the control. Addition of 250 µg/ml of Gd(OH)₃:Eu³⁺ induced an increase of dead cells to 6.51%. Fluorescence microscopy images of A549 cells after 24 h incubation with Gd₂O₃:Eu³⁺ and Gd₂O₃:Eu³⁺ (c = 250 µg/ml) are shown in Figure 9.

Figure 9. Effect of Eu³⁺ doped gadolinium hydroxide and Eu³⁺ doped gadolinium oxide nanostructures on the viability of A549. Cells were treated with 250µg/ml Eu³⁺ doped gadolinium-containing nanostructures. Fluorescence microscopic images of A549 cells after 4h and 24h of exposure were taken after staining the cells with fluorescein diacetate (FDA) and propidium iodide (PI). Dead cells were stained red (PI), viable cells were stained green (FDA). A549 cells were exposed to: (A) nanostructures-free cell culture medium as negative control, scale bar 50µm, (B) Eu³⁺-doped gadolinium hydroxide nanostructures, scale bar 20µm. (C) TritonX-100 2% as positive control, scale bar 50µm. (D) Eu³⁺-doped gadolinium oxide nanostructures, scale bar 20µm.

The metabolic activity, proliferation rate and membrane integrity of the cells exposed to the nanostructures were similar to those observed in the control sample incubated with a nanostructure-free suspension, which means that Gd(OH)₃:Eu³⁺ and Gd₂O₃:Eu³⁺ nanostructures are biocompatible at the tested concentrations in A549 cells. According to the described investigations Gd(OH)₃:Eu³⁺ as well as Gd₂O₃:Eu³⁺ nanostructures did not appear to be toxic in human lung epithelial cells (A549) at concentrations up to 250 µg/ml (Figure 6, 7 and 8). Previous investigations by our group have shown that Gd(OH)₃:Eu³⁺ and Gd₂O₃:Eu³⁺ nanostructures were also biocompatible in human colon carcinoma cells (Caco2). Therefore we can conclude that the Eu³⁺ doped nanostructures do not induce remarkable cytotoxicity under given circumstances, neither in A549 cells nor in Caco2 cells till the concentration of 250 µg/ml.
Conclusion

The interest of this study lied in the preparation of Eu\(^{3+}\) doped nanostructures, with respect of future applications in biomedical diagnostics. Therefore, Eu\(^{3+}\) doped Gd(OH)\(_3\) and Eu\(^{3+}\) doped Gd\(_2\)O\(_3\) nanostructures were prepared by solvothermal synthesis. The obtained powders were investigated with regard to their morphology, elemental composition and photoluminescence. As-prepared undoped Gd(OH)\(_3\) powders showed a rod-like morphology with an aspect ratio in the range of 15 to 20, while doped hydroxides, as well as post-annealed oxide powders revealed an inhomogenous microstructure. Emission properties of Eu\(^{3+}\) doped samples were investigated by photoluminescence spectroscopy showing the characteristic peaks due to f-f transition of Eu\(^{3+}\) in the red range of the visible spectrum. Cell proliferation, metabolic activity as well as the membrane integrity after different exposure times (4 and 24 h) were investigated using human lung carcinoma as test system. Eu\(^{3+}\) doped Gd(OH)\(_3\) and Eu\(^{3+}\)-doped Gd\(_2\)O\(_3\) nanostructures showed no cytotoxicity up to 250 µg/ml. The observed biocompatibility of the doped nanostructures makes Eu\(^{3+}\) doped Gd-containing nanostructures promising candidates for more sensitive diagnostic tools which may overcome the problems of recently used systems.

Experimental Section

Synthesis and characterization of Eu\(^{3+}\) doped Gd(OH)\(_3\) and Gd\(_2\)O\(_3\) nanostructures

Gadolinium oleate, Gd(C\(_{18}H_{33}O_2\))\(_3\), was used as precursor in solvothermal synthesis for the preparation of Gd(OH)\(_3\) nanostructures.\(^{31}\) The gadolinium oleate complex was obtained by salt elimination reaction of gadolinium chloride hexahydrate (2.5 mg, 6.8 mmol) with sodium oleate (6.2 mg, 20.3 mmol) as a colorless waxy solid as described in the literature.\(^{32,33}\) The results of elemental analysis are in good agreement with calculated carbon and hydrogen contents (C: 62.76 % / calculated: 64.75 %, H: 10.12 % / calculated: 9.96 %). The recorded FT-IR spectrum (Vektor 22 spectrometer by Bruker) showed sharp peaks in the range from 1650 to 1510 cm\(^{-1}\) which are characteristic for metal-carboxylate vibrations and confirm the formation of the desired compound. For solvothermal decomposition of the gadolinium oleate complex 200 mg of the compound were dissolved in 20 ml hexane followed by pre-hydrolysis with aqueous potassium hydroxide solution (V = 1 ml, c = 1.87 mol/l). The activated solution was transferred into Teflon liners (V = 50 ml), which were closed in stainless steel autoclaves (DAB-2, Berghof Products & Instruments GmbH), the temperature was raised to 250 °C and kept for 24 h. After cooling to room temperature obtained precipitates were washed several times with methanol and ethanol, collected by centrifugation and dried under ambient conditions. Doping of Gd(OH)\(_3\), with Eu\(^{3+}\) ions was achieved by dispersing 250 mg (1.2 mmol) of as-prepared gadolinium hydroxide in 10 ml water, followed by the addition of 10 ml of an aqueous solution of EuCl\(_3\)-6H\(_2\)O (43.98 mg, 0.12 mmol, doping rate: 10 mol%). 1,2-ethanediol (13.38 ml, 0.24 mmol) as complexing agent was added to the above solution.\(^{34}\) The solution was concentrated by slow evaporation at 60 °C with stirring resulting in a white gel, which was ground and annealed in air at 600 and 1100 °C during 2 h.

All powders were characterized by powder X-ray diffraction with regard to their crystallinity and phase (X-ray diffractometer ULTIMA III, Rigaku) using CuK\(_{α1}\) radiation as the X-ray source. For FT-IR spectroscopy of the obtained materials powders were mixed with KBr and spectra were recorded under vacuum conditions using a Jasco FT/IR-6200 spectrometer. Scanning electron microscopy (S-4200, Hitachi) and transmission electron microscopy (JEOL 200 CX, Philips) were used for investigation of morphology. Optical properties of the europium-doped samples were analyzed in a RF-5000 spectrofluorophotometer by Shimadzu-Seisakusho recording emission and excitation spectra at room temperature.

Cell culture and exposure to nanostructures

For the cytotoxicity studies A549 cells were used. The A549 cell line (ATCC, LGC Promochem, Germany) is a human lung carcinoma epithelial cell line. The cell line was cultured in RPMI 1640 without L-glutamine, supplemented with penicillin/streptomycin, sodium pyruvate, glucose and 10% foetal calf serum (FCS). To monitor the cytotoxic effect of the nanostructures 1 x 10\(^4\) cells/well were seeded in a 96 well micro titre plate. At day two, when the cells were adherent they were washed one time with PBS and incubated with different concentrations in the range of 0-250 µg/ml over 4 and 24 h. The final concentrations 50 µg/ml and 250 µg/ml were adjusted by dilution of the prepared nanostructures in cell culture medium. Each cytotoxicity experiment included a positive control, which was Triton X 2%, and nanostructures-free cell culture medium as a negative control.


© 2010 NWT-Verlag, Bornheim, Germany
**WST-1 assay (Mitochondrial function).** The mitochondrial function of the cells exposed to the nanostructures was analyzed using the WST-1 assay (Roche Diagnostics, Mannheim, Germany). WST-1 assay was performed after 4 h and 24 h according to manufacturer’s instructions, with appropriate controls. After exposure to nanostructures the cells were incubated with the ready-to-use WST-1 reagent for 4 h. Thereafter the absorbance was quantified at 650 nm using scanning multi-well spectrophotometer reader (Tecan, Crailsheim, Germany). The measured absorbance directly correlates to the number of viable cells.

**BrdU assay (Cell proliferation rate).** The detection of the proliferation rate of the cells exposed to nanostructures was performed using the BrdU assay kit by Roche Diagnostics (Mannheim, Germany), according to manufacturer’s instructions, with appropriate controls. The reaction product is quantified by measuring the absorbance using a scanning multi-well spectrophotometer (ELISA reader). The measured absorbance directly correlates to the number of viable cells.

**LDH assay (Membrane integrity).** To detect the membrane integrity of the cells exposed to the nanostructures, lactate dehydrogenase (LDH) release was monitored. In the used LDH assay (Roche Diagnostics, Mannheim, Germany), LDH released from damaged cells oxidizes lactate to pyruvate, which promotes conversion of tetrazolium salt into formazan, a water-soluble molecule with absorbance at 490 nm. 4 and 24 h after nanorod exposition the supernatant of the cells was transferred in a new 96 well micro titre plate and mixed with the corresponding volume of LDH reagent. The formazan dye was quantified using scanning multi-well spectrophotometer reader (Tecan, Crailsheim, Germany). The amount of LDH release is proportional to the number of cells damaged or lysed.

**Living/Dead staining.** To detect the percentage of viable and dead cells, a dye mixture of fluoresceine diacetate (FDA) and propidium iodide (PI) was employed to stain the cells. The cells were grown in a cell culture dish (35/10 mm, Greiner Bio One, Germany). Cell culture medium containing nanomaterial was incubated for 4 and 24 h. Afterwards, the cells were treated with the fluorescent dye mixture and observed via confocal fluorescence microscope (Zeiss, Germany). Living cells show green fluorescence, while dead cells show a red fluorescence signal.

**Acknowledgements**

This work has been supported by the German Science Foundation (DFG) in the frame of the Priority Program “Lanthanide specific functionalities in molecule and material” (SPP-1166). The authors thank Wuerzburg University, Government of Saarland and Leibniz Society for the provision of the infrastructure allowing the realization of this work. Our special thanks are due to Dr. H. Shen (University of Cologne) for TEM images.

Received: December 21, 2009.

© 2010 NWT-Verlag, Bornheim, Germany