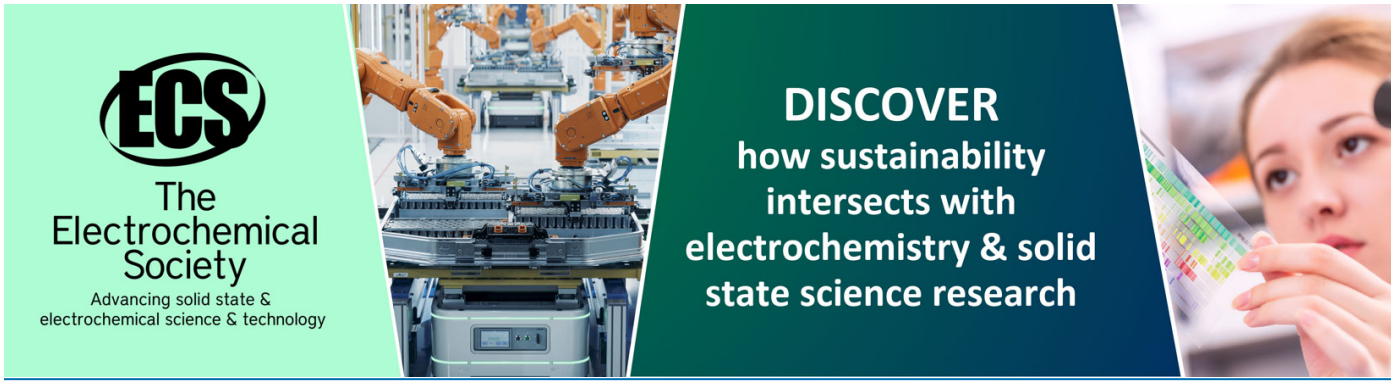
Europium-doped Lu2O3 phosphors prepared by a sol-gel method



Europium-doped Lu2O3 phosphors prepared by a sol-gel method

T Thoř[1], K Rubešová[1], V Jakeš[1], J Cajzl[1], L Nádherný[1], D Mikolášová[1], A Beitlerová[2] and M Nikl[2]

[1] Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic
[2] Institute of Physics of the Czech Academy of Sciences, Cukrovarnická 10, 162 53 Prague 6, Czech Republic

Tomas.Thor@vscht.cz

Abstract. Cubic lutetium sesquioxide (Lu2O3) presents a suitable host material because of its favourable properties including chemical and phase stability. Lu2O3 has a wide band gap (> 5.5 eV) and its doping with lanthanide ions, which behave as activators, gives rise to some unique optical properties. Also, due to a high effective atomic number (Zeff = 68.8) and high density (9.42 g/cm3) of the Lu2O3 host, providing high stopping power for ionizing radiation, it has also attracted attention as a scintillator material. Since optical properties are affected by both crystal structure and morphology, which depend strongly on the synthesis method and conditions employed, many different methods have been studied for its synthesis. However, due to high melting temperature of Lu2O3 (2490 °C), the preparation of single crystals is difficult. In our work, we prepared polycrystalline samples of Eu:Lu2O3 using a sol-gel route based on the Pechini polycondensation. We tested three europium doping concentrations, two different annealing regimes were examined as well. The influence of mentioned parameters on photoluminescent and radioluminescent properties was established. Our samples proved that the used synthesis method can be used for further research of Lu2O3 doped with other rare-earth metals.

1. Introduction

Lutetium oxide is a phosphor material, whose emission properties can be tuned and enhanced by incorporating suitable dopants into its structure. As such it can find use in different lightning related applications, such as fluorescent lamps, cathode ray tubes or plasma display panels [1–3]. Furthermore, thanks to its high density of 9.42 g/cm^3 and high effective atomic number (Z_{eff} = 68.8), prompting high stopping power for ionizing radiation, it can also serve as a scintillating material (doped and even un-doped), converting high energy ionizing radiation to UV-Vis photons [4]. Lutetium oxide crystalizes in a bixbyite type cubic structure. Its crystal cell consists of a total of 32 cation sites, from which 24 show the low-symmetry C_2 point group and the remaining 8 show inversion symmetry having the C_{3i} (S_6) point group [5]. The inversion symmetry of the S_6 site leads to significantly lower cross section for dopant ions implemented on this site compared to those ions on C_2 sites. Therefore optical properties of doped Lu_2O_3 are dominated by dopant ions occupying low symmetry C_2 sites [6,7]. However, the way

in which these sites are filled with dopant cations is not yet fully understood and therefore it is often approximated as a random process.

Lutetium oxide possesses a high melting point of 2490 °C. On one hand, this empirically points towards a high chemical and mechanical stability, on the other hand, it makes the fabrication very difficult [6]. Such extremely high temperature presents a significant challenge for single crystal growth processes. Therefore, other methods have been studied for its fabrication, such as precipitation [8–11], combustion synthesis [12], polymer complex solution method [13], flame spray pyrolysis [14] or the sol-gel route [15].

In this work, we used the Pechini-type sol-gel method to prepare a series of europium-doped lutetium oxides. Europium ions act as an activator in Lu_2O_3 host, having the energy levels in the band gap of Lu_2O_3 and exhibiting a characteristic emission in the visible region of electromagnetic spectrum. The concentration of europium was selected based on published optimal concentration of europium in a very similar yttrium oxide host [16,17]. Then we prepared three samples with the concentration interval around the optimized one: $Eu_xLu_{(2-x)}O_3$, where x = 0.1, 0.15 and 0.2, corresponding to 5%, 7.5% and 10% Eu^{3+} doping, respectively. We used two different regimes for the final heat treatment, 1000 °C/4 h and 1250 °C/24 h, and its influence on the studied luminescence properties was established.

2. Materials and methods

2.1. Bulk samples preparation

Lutetium oxide (Crytur Turnov; 99.99 % (REO)) was first dissolved in HNO3 (Penta; 65 %; p.a.) in a molar ratio of 1 mol Lu : 3.5 mol HNO3. Concentrated HNO3 was diluted with water in a volume ratio of 1:2. Mixture was stirred at 60 °C until clear solution was formed. Then europium acetate Eu(O2CCH3)3 (Strem chemicals; 99.9 % (REO)) was added to this solution. After dissolving, citric acid (CA; Lach:ner; anhydrous; p.a.) was added to the solution together with additional water required for a saturated solution of CA. The molar ratio of metal cations:CA was 1:4. Ethylen glycol (EG; Penta; 99 %) was added to the solution with the ratio of metal:EG being 1:16. The resulting solution was stirred at 80 °C until water was evaporated. Temperature was further increased to initiate polycondensation leading up to gelation. As prepared gel was dried at 250 °C in air for two hours. Dried xerogel was then subjected to a series of thermal treatments: first at 500 °C for 2 hours with 3 hours long ramp, then at 900 °C for 2 hours with 1.5 hours long ramp and rapid cooling at the end. Before the final heat treatment, powder samples were pressed into 1x2x10 mm pellets. The final annealing was performed in two regimes: 1000 °C for 4 hours and 1250 °C for 24 hours.

2.2. Characterization methods

X-ray powder diffraction (XRD) data were collected at room temperature with Bruker AXS D2 Phaser powder diffractometer with parafocusing Bragg-Brentano geometry using CoK_α radiation. Data evaluation was performed in the software package HighScore Plus (Malvern Panalytical).

The steady-state photoluminescence properties of the prepared samples were measured on a HORIBA Jobin Yvon Fluorolog®-3 Extreme spectrometer using FluorEssence™ 3 software. The spectra were collected at room temperature within the range of 450–800 nm. A photomultiplier tube (PMT) with thermoelectric cooling and a Ce:InGaAs photocathode (model number R955, detection range 185–900 nm) were used. Sample excitation was performed using a 450 W xenon continuous-wave (CW) lamp. To select various wavelengths, a double-diffraction-grating monochromator at the entrance and a single-diffraction-grating monochromator at the exit were used. The photoluminescence spectra were collected in a reflective arrangement with the sample being tilted at angle of approx. 60°. The photoluminescence radiation was collected at the front-facing exit. For the spectra evaluation, all of the measured luminescence spectra were transformed to the base level and, after subtraction of the background, normalised with the help of a reference sample (a single crystal of Ce:YAG).

The radioluminescence spectra were measured at room temperature. The custom made 5000M Horiba Jobin Yvon fluorescence spectrometer with a TBX-04 photon counting detector (IBH Scotland) was used. The samples were excited by an X-ray (40 kV,15mA) tube (SeifertGmbh). All spectra were corrected for the spectral distortions due to the setup. Spectral resolution used in the radioluminescence spectra measurements was 8 nm.

3. Results and discussion

Two series of europium-doped Lu_2O_3 were prepared using two different annealing temperatures (1000 °C or 1250 °C). Within each series, three samples with different europium doping were prepared - $Eu_xLu_{(2-x)}O_3$, where x = 0.1, 0.15 and 0.2, which corresponds to 5%, 7.5% and 10% Eu^{3+} doping, respectively.

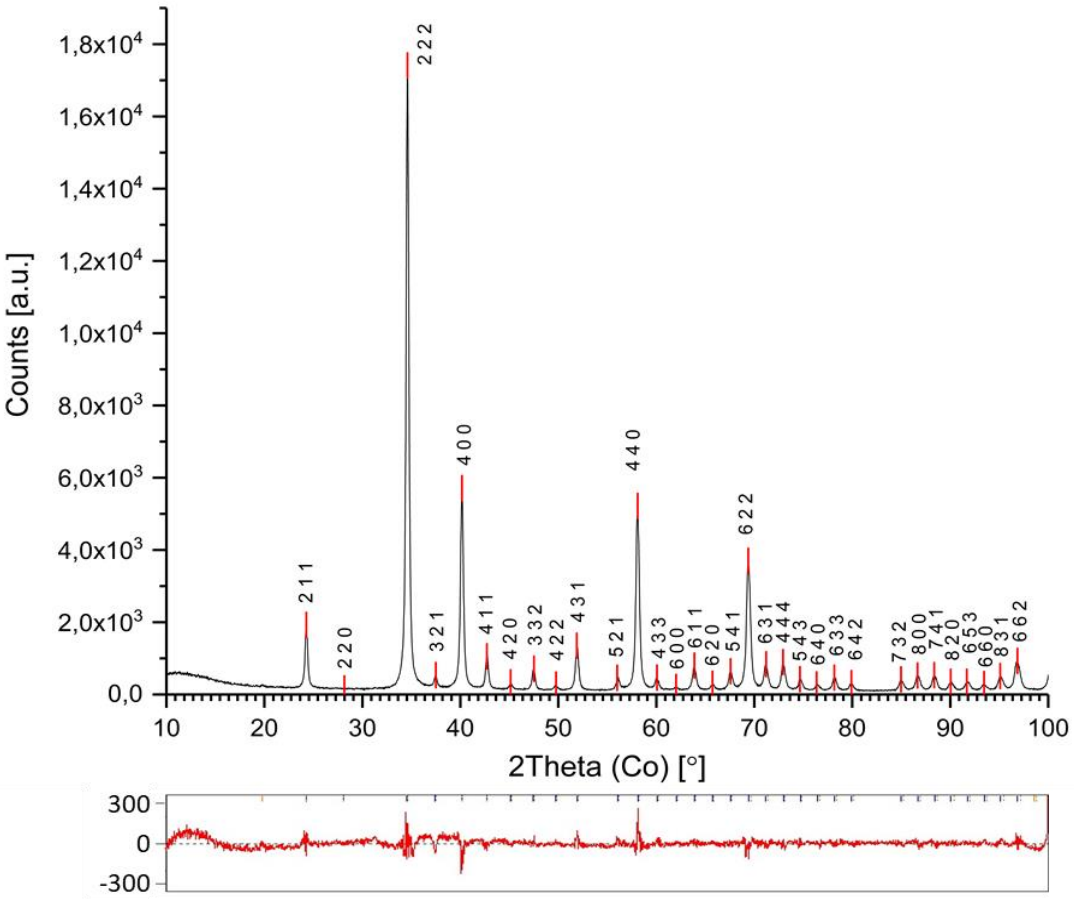


Figure 1: XRD pattern and difference plot of $Eu_{0.15}Lu_{1.85}O_3$ annealed at 1000 °C.

X-ray diffraction measurement showed that all of europium-doped Lu_2O_3 samples were single phase. As shown in the case of $Eu_{0.15}Lu_{1.85}O_3$ in figure 1, all of reflections in XRD pattern can be assigned to a cubic bixbyite type structure of un-doped Lu_2O_3, according to PDF 01-086-2475. Even for the highest concentration of europium used, no minor phase was detected. However, the europium doping influenced the unit cell size. After the Pawley fitting of XRD patterns, the unit cell parameter *a* was determined. In the scope of concentrations used, the dependence of lattice parameter on Eu concentration was observed to be linear (figure 2). Because of the effect of lanthanide contraction, ionic radii of europium ions are higher than in the case of lutetium ions, and thus substituting europium into a lutetium oxide host leads to an increase of lattice parameter. In terms of different annealing temperatures used,

samples annealed at higher temperatures showed sharper diffraction peaks with smaller FWHM, which can be attributed to better crystallinity of those samples.

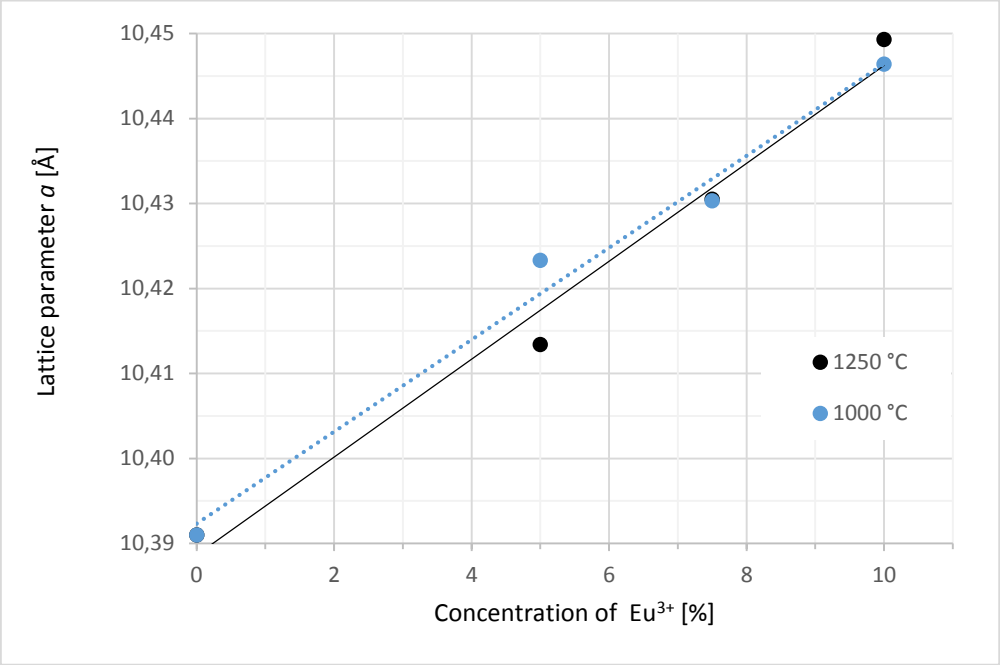


Figure 2. Lattice parameter of Eu:Lu2O3 as a function of increasing concentration of Eu3+ ions.

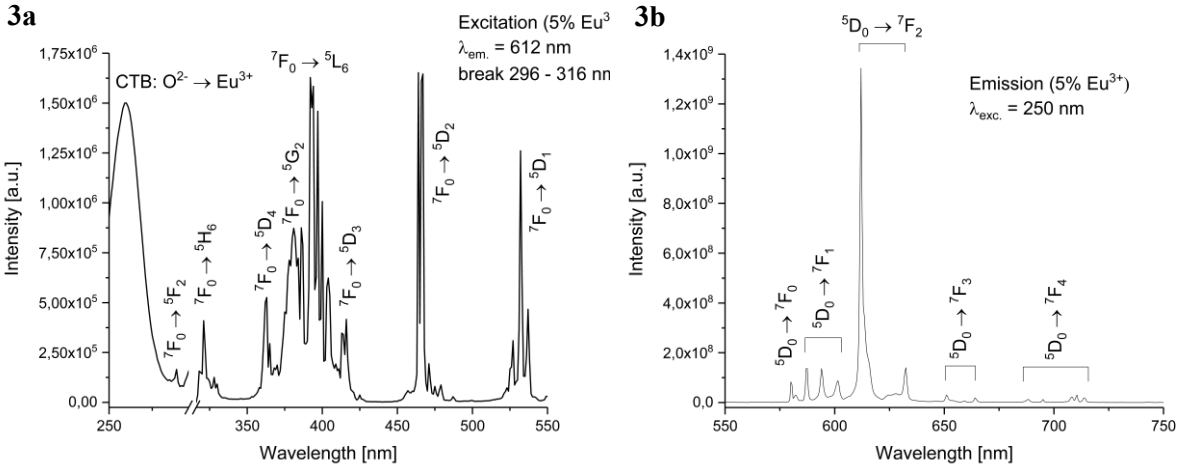


Figure 3. Photoluminescence excitation (3a) and emission (3b) spectra of $Eu_{0.1}Lu_{1.9}O_3$ annealed at 1250 °C.

The photoluminescence excitation spectrum of Eu:Lu2O3 (figure 3a) shows a broad band at around 260 nm corresponding to the charge transfer band from O2-(2p) to Eu3+(4f). Other bands shown correspond to 4f-4f transitions of Eu3+ from the 7F0 ground state to higher levels. Due to instrumentation issues, we could not filter harmonic excitation, therefore data around that were cut out using axis break.

The emission spectrum of Eu:Lu2O3 (figure 3b) reflects the transitions from the excited 5D0 level to the 7FJ (J = 0, 1, 2, 3, 4) levels of Eu3+. The most intense line, centred around 612 nm, corresponds to the hypersensitive transition to the 7F2 energy level. This emission is assigned to Eu3+ ions on the C2 sites in the Lu2O3 host [18]. However, all emission bands show narrow band width demonstrating homogeneous distribution of the dopant within the Lu2O3 host having good crystallinity.

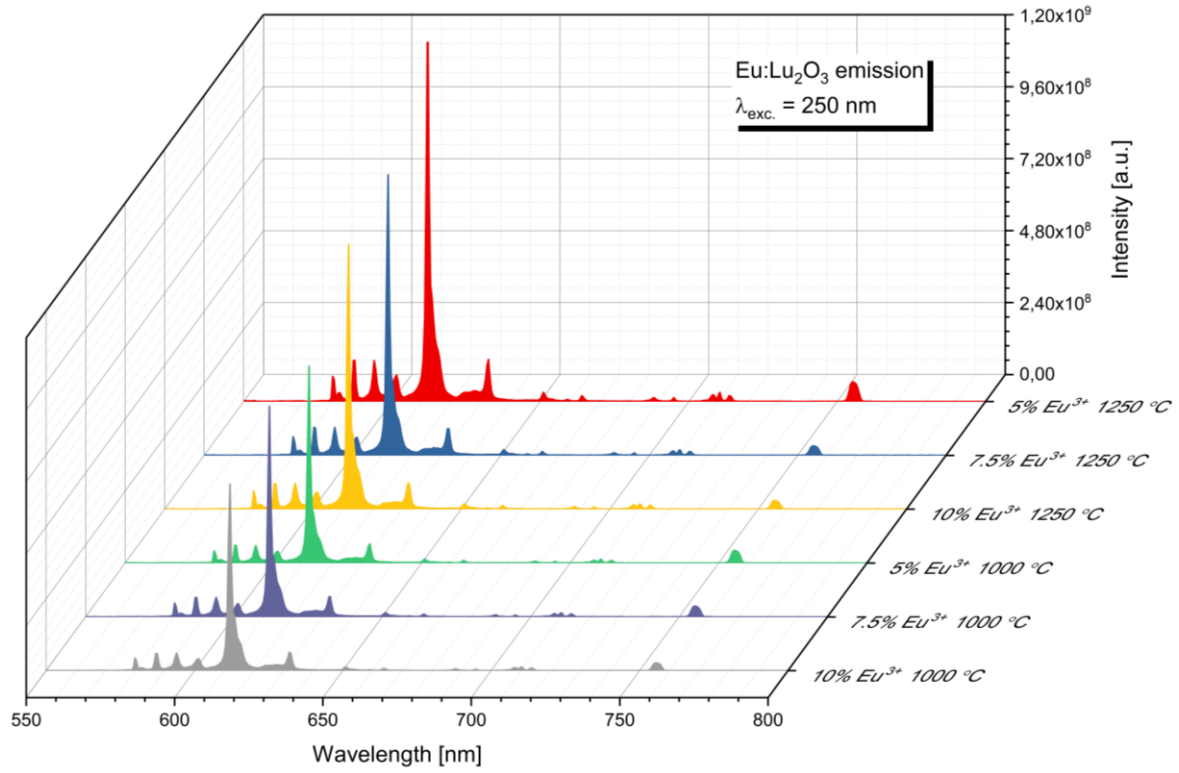


Figure 4: Photoluminescence emission spectra of $Eu_xLu_{(2-x)}O_3$ samples annealed at 1000 °C and 1250 °C.

Figure 4 shows photoluminescence emission spectra of samples with different dopant concentration and annealing temperature. Comparing overall photoluminescence emission intensity, it was higher in the case of samples annealed at higher temperature. This is most probably connected with the improvement of Lu2O3 host crystallinity and the better crystal vicinity of dopant ions. For the samples annealed at 1000 °C, the intensity increases slightly with dopant concentration from 5 to 7.5% and then slightly decreases for 10% Eu3+ concentration, most likely due to concentration quenching phenomenon caused by cross-relaxation between neighbouring Eu3+ ions. For the samples annealed at 1250 °C we can see different trend, since the highest intensity is observed for 5% of Eu3+ and then drops with the increasing concentration of Eu3+.

Although worse in resolution, radioluminescence spectra (figure 5) resemble closely photoluminescence emission spectra. Again, in all the samples, the emission pattern matches fully the emission of Eu3+ 4f-4f transitions, with the most intense one at 612 nm belonging to the 5D0 □ 7F2 energy transfer. For lower annealing temperature (1000 °C), the emission intensity increases monotonically with Eu concentration and further increases when the higher temperature of annealing was used. Within the 1250 °C series, the highest emission intensity was measured for 7.5% of Eu; however, the difference between 5% and 7.5% was negligible. 10% of Eu caused the decrease of the radioluminescence intensity. Despite the polycrystalline character of our samples, the measured radioluminescence intensity was by several orders of magnitude higher than for the reference BGO (bismuth germanate) single crystal (the red line in figure 5).

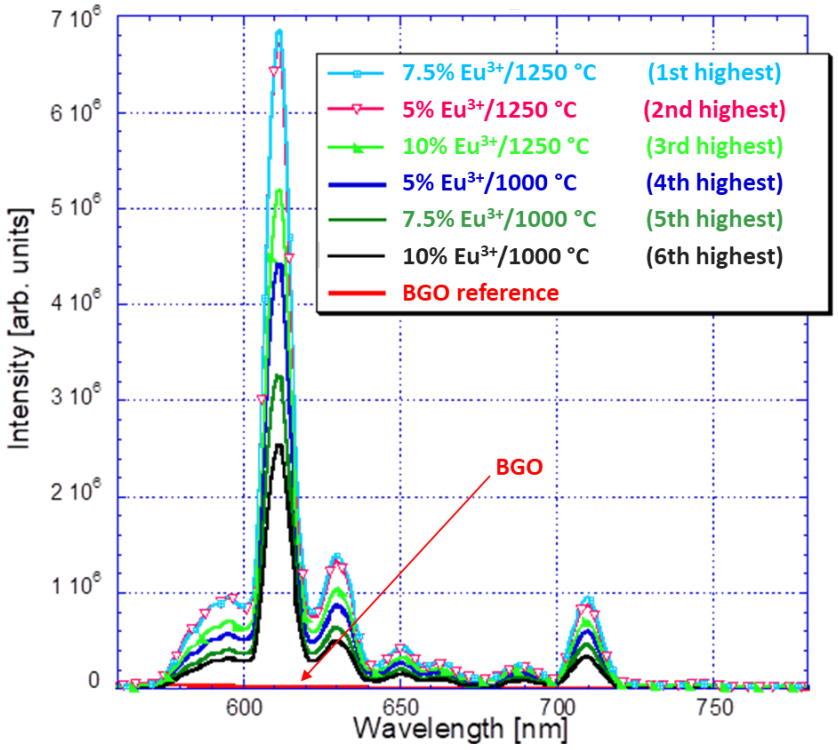


Figure 5. Radioluminescence spectrum of $Eu_xLu_{(2-x)}O_3$ (also the reference spectrum of BGO standard is included).

4. Conclusions

Lutetium oxide presents suitable host for the use either in phosphors or in scintillation applications. Here, we tested Eu-doped Lu_2O_3 prepared in a polycrystalline form. The dopant ions were successfully incorporated into Lu_2O_3 host for all concentrations used, not causing any phase changes. Photoluminescence and radioluminescence emission spectra were dominated by the f-f transitions of Eu^{3+} ions. Concentration quenching was clearly present for some doping concentrations and was probably caused by cross-relaxation processes in ion pairs. Annealing at higher temperature (1250 °C) increased both photoluminescence and radioluminescence emission intensities, most probably due to better crystallinity of the Lu_2O_3 host. The presented samples show that polycrystalline Lu_2O_3 can be successfully used for the further research of lanthanide dopants never previously examined.

Acknowledgment

This work was financially supported by specific university research (MSMT No 20-SVV/2017) and by the TA CR, project No. TJ0100041

References

[1] Yang J and Lin J 2010 Sol-Gel Synthesis of Nanocrystalline Yb3+/Ho3+-Doped Lu2O3 as an Efficient Green Phosphor *J. Electrochem. Soc.* **157** K273

[2] Boyer J C, Vetrone F, Capobianco J A, Speghini A and Bettinelli M 2004 Variation of Fluorescence Lifetimes and Judd-Ofelt Parameters between Eu3+ Doped Bulk and Nanocrystalline Cubic Lu2O3 *J. Phys. Chem. B* **108** 20137

[3] Zhang H, Chen J and Guo H 2010 Electrospinning synthesis and luminescent properties of

Lu2O3:Eu3+ nanofibers *J. Rare Earths* **28** 232
[4] Dujardin C, García Murillo A, Pedrini C, Madej C, Goutaudier C, Koch A, Petrosyan A G, Ovanesyan K L, Shirinyan G O and Weber M J 2000 Synthesis and scintillation properties of some dense X-ray phosphors *Proc. Int. Conf. Inorg. Scintill. Their Appl. SCINT99* 527
[5] Chen X, Xiang G, Chai F, Zhang Z, Shi S, Xu F and Zhao J 2016 An alternate spin-coating strategy toward high-quality polycrystalline thin Lu2O3: Eu3+ film fabrication *Surf. Coat. Technol.* **302** 523
[6] Kränkel C 2015 Rare-Earth-Doped Sesquioxides for Diode-Pumped High-Power Lasers in the 1-, 2-, and 3- µm Spectral Range *IEEE J. Sel. Top. Quantum Electron.* **21** 250
[7] Concas G, Spano G, Zych E and Trojan-Piegza J 2005 Nano- and microcrystalline Lu 2 O 3 :Eu phosphors: variations in occupancy of C 2 and S 6 sites by Eu 3+ ions *J. Phys. Condens. Matter* **17** 2597
[8] Lu B, Li J-G and Sakka Y 2013 Controlled processing of (Gd,Ln)2O3:Eu (Ln = Y, Lu) red phosphor particles and compositional effects on photoluminescence *Sci. Technol. Adv. Mater.* **14** 064202
[9] Dulina N A, Baumer V N, Danylenko M I, Mateyehenko P V, Tolrnachev A V, Vovk O M and Yavetskiy R P 2013 Effects of phase and chemical composition of precursor on structural and morphological properties of (Lu0.95Eu0.05)(2)O-3 nanopowders *Ceram. Int.* **39** 2397
[10] Marton Z, Bhandari H B, Brecher C, Miller S R, Singh B and Nagarkar V V 2013 Fabrication of High-Resolution Lu2O3:Eu X-Ray Scintillator by Physical Vapor Deposition *Ieee Trans. Nucl. Sci.* **60** 983
[11] Kopylov Y L, Kravchenko V B, Dulina N A, Lopin A V, Parkhomenko S V, Tolmachev A V, Yavetskiy R P and Zelenskaya O V 2013 Fabrication and characterization of Eu3+-doped Lu2O3 scintillation ceramics *Opt. Mater.* **35** 812
[12] Seferis I, Michail C, Valais I, Zeler J, Liaparinos P, Fountos G, Kalyvas N, David S, Stromatia F, Zych E, Kandarakis I and Panayiotakis G 2014 Light emission efficiency and imaging performance of Lu2O3:Eu nanophosphor under X-ray radiography conditions: Comparison with Gd2O2S:Eu *J. Lumin.* **151** 229–34
[13] Whiffen R M K, Antic Z, Speghini A, Brik M G, Bartova B, Bettinelli M and Dramicanin M D 2014 Structural and spectroscopic studies of Eu3+ doped Lu2O3-Gd2O3 solid solutions *Opt. Mater.* **36** 1083
[14] Seeley Z M, Dai Z R, Kuntz J D, Cherepy N J and Payne S A 2012 Phase stabilization in transparent Lu2O3:Eu ceramics by lattice expansion *Opt. Mater.* **35** 74
[15] de Jesus Morales-Ramirez A, Garcia-Murillo A, de Jesus Carrillo-Romo F, Garrido-Hernandez A and Garcia-Hernandez M 2015 Influence of annealing temperature on structural and optical properties of Lu2O3:Eu3+, Tb3+ transparent films *Mater. Res. Bull.* **70** 173
[16] Hao B V, Huy P T, Khiem T N, Ngan N T T and Duong P H 2009 Synthesis of Y2O3:Eu3+ micro- and nanophosphors by sol-gel process *J. Phys. Conf. Ser.* **187** 012074
[17] Alarcón-Flores G, García-Hipólito M, Aguilar-Frutis M, Carmona-Téllez S, Martinez-Martinez R, Campos-Arias M P, Zaleta-Alejandre E and Falcony C 2015 Synthesis and fabrication of Y2O3:Tb3+ and Y2O3:Eu3+ thin films for electroluminescent applications: Optical and structural characteristics *Mater. Chem. Phys.* **149** 34
[18] Pedroso C C S, Carvalho J M, Rodrigues L C V, Holsa J and Brito H F 2016 Rapid and Energy-Saving Microwave-Assisted Solid-State Synthesis of Pr3+-, Eu3+-, or Tb3+-Doped Lu2O3 Persistent Luminescence Materials *Acs Appl. Mater. Interfaces* **8** 19593