The impact of doping concentration on structure and photoluminescence of Lu_2O_3:Eu^{3+} nanocrystals

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ARTICLE INFO

ABSTRACT

Cubic Eu^{3+}-doped Lu_2O_3 nanocrystals were synthesized via combined Pechini-foaming method. Doping concentration effect on the structural and luminescence properties was studied. It was found that the increase of Eu^{3+} concentration leads to the growth of unit cell parameters and red shift of Raman lines. The optimal doping concentration and shape of emission lines were studied upon different excitation mechanism. Radiative and nonradiative transition rates and Judd-Ofelt parameters were calculated using the model of 4f–4f intensity theory. The type of multipolar interaction resulting in luminescence concentration quenching was determined.

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1. Introduction

Nanosized materials doped with rare earth ions have attracted extensive attention in the past few decades due to their unique electronic and optical properties and potential applications in the fields of high-performance luminescence devices, magnets, catalysts, medical diagnostics, biological fluorescence labels, etc. [1–5]. Such phosphors often demonstrate significant changes in their properties compared with bulk materials due to the increase of surface/volume ratio and as a result enhancement of surface role [6–8].

Rare earth oxides are widely used as a host lattice for active ion introduction [9–11]. Among them, lutetium oxide attracts increasing attention because of its high density (9.4 g/cm³), high atomic number ($Z=71$), high physical and chemical stability, and a band gap large enough to accommodate the energy levels of many luminescent activator [12]. In addition, Lu_2O_3 has the same cubic structure as Y_2O_3, a well-known host lattice for efficient, commercial phosphors. It was reported that Eu^{3+} doped lutetia is promising scintillator, especially for medical use [13], therefore it is important to synthesize and study this material.

Nowadays, there are a large variety of approaches to produce nanosized phosphors doped with rare earth ions with controlled chemical-physical parameters. One of the most cheap and easy way to synthesize nanocrystalline powders is Pechini technique [14]. The main disadvantage of standard Pechini technique is strong agglomeration of derived particles. To overcome this drawback and to improve properties of the obtained nanopowders, we have developed combined Pechini-foaming method applicable for synthesis of simple oxides.

Despite wide application of Eu^{3+} doped Lu_2O_3 particles and numerous papers devoted to the research of this material, to the best of our knowledge, there is a lack of studies dealing with wide concentration series and luminescence quenching in lutetia host.

The aim of this work is to provide the systematic study of doping concentration effect on the structural and luminescence properties of nanocrystalline Lu_2O_3:Eu^{3+} powders. Analysis of the optimum concentration dependence upon excitation wavelength and determination of the concentration quenching mechanism were also performed.

2. Experimental

Eu^{3+} doped Lu_2O_3 nanopowders were prepared by the combined Pechini-foaming method. Previously we synthesized complex oxides doped with different rare earth ions using modified Pechini method [15–17]. This method reduces agglomeration but requires two calcination stages.

The proposed combined technique is also an improved standard Pechini method but it has only one calcination stage. The main part of modification is implementation of foaming agent into polymer gel matrix in order to prevent strong agglomeration of synthesized samples. Unlike Y_2O_3:Eu^{3+} concentration series [18], we used potassium carbonate as a foaming agent.

Solutions of lutetium and europium nitrates were used as precursors. The nitrates had been obtained by dissolving their oxides in concentrated nitric acid. The solutions of the nitrates mixture were heated and then the saturated solution of citric acid was added to the solutions in volume ratio 1:1. The chemical reaction equation can be represented as:

$$Me(NO_3)_3 + 3C_6H_8O_7 = \left[Me(C_6H_8O_7)_3 \right](NO_3)_3$$
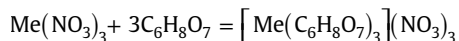
Then potassium carbonate was also added to the solution (weight ratio of the potassium carbonate to the final oxide powder was 1:1). Addition of the ethylene glycol to the metals complexes (volume ratio of the ethylene glycol solution to the citric acid solution was 1:4) leads to the transparent polymer gel formation due to etherification reaction. Pores of the polymer were filled by the potassium carbonate solution. The obtained polymer was annealed at 1000 °C during 90 minutes to remove organic components. The synthesized particles were collected by centrifugation at 2800 rpm for 5 min; repeated 3 times. The resulting washed precipitate was dried in an oven at 110 °C.

The described method was used to synthesize wide concentration series of Lu_2O_3:Eu^{3+} (2–40 at%). The synthesized powder samples (5 mg) and potassium bromide (300 mg) were pressed into pellets (diameter 13 mm) for luminescence studies.

X-ray diffraction patterns were registered with the powder diffractometer UltimaIV (Rigaku) in Bregg-Bretano geometry with CuKα1 radiation (λ=1.54059 Å) in the 2θ range from 10° to 80°. Phase identification was carried out using a powder diffraction database PowderDiffractionFile (PDF-2, 2011). The unit cell parameters were estimated using TOPAS software by full-profile analysis. Electron micrograph images were obtained with Zeiss Supra 40VP scanning electron microscope (resolution 4 nm). Raman spectra were measured with LabRAM with argon laser (λ=488 nm) as an excitation source. Luminescent spectra were recorded with a fluorescence spectrometer Fluorolog-3 equipped with a Xe-arc lamp (450 W power). For the lifetime measurements the europium luminescence was excited with a Xe-flash lamp (150 W power, 3 μs pulse width). All the measurements were performed at the room temperature.

3. Results and discussion

3.1. Structural analysis

Fig. 1a presents XRD patterns of Lu_2O_3:Eu^{3+} nanophosphors series with doping concentration C(Eu^{3+})=2–40 at%. All observed peaks in diffraction patterns match well to cubic phase of Lu_2O_3 (JCPDS 43-1021). It can be clearly seen that diffraction lines position significantly shifts towards a lower angle along with doping concentration increase.

The unit cell parameters were calculated with TOPAS software using full-profile analysis. According to calculations, both unit cell parameter and single-crystal cell volume systematically increase with growth of Eu^{3+} ions concentration. This fact can be explained by substitution of lutetium ions (r=0.86 Å) with larger europium ions (r=0.95 Å) [19]. It should be noted that the cell volume has a linear relationship with the content of Eu^{3+}, which is consistent with Vegard's law (Fig. 1b). This result demonstrates that the europium ion has been efficiently and homogeneously incorporated into the host matrix due to the similar ionic radius and chemical reactivity of Eu^{3+} and Lu^{3+}. So, the obtained results testify that the doping ions occupy lutetium sites in crystal lattice.

SEM image of Lu_2O_3:Eu^{3+} 2 at% nanocrystalline powder is shown in Fig. 2. It can be seen, that obtained powder consists of rather small well-faceted nanoparticles. The average size of these nanoparticles was determined to be about 45 nm with standard deviation of 16 nm.

Fig. 3a presents Raman spectra of Lu_2O_3:Eu^{3+} nanopowders with various doping concentration normalized to the band centered at about 390 cm^{-1} and measured in the spectral region of 80–700 cm^{-1}.

According to the factor group theory investigation [20], twenty two Raman modes have been predicted for the cubic lutetia lattice belonging to the $Ia3$ space group with C type structure.

The major Raman peak is observed at about 391 cm^{-1} and can be assigned to $F_g + A_g$ mode [21]. The high intensity of this band compared to the others indicates a large polarizability variation during the vibration [21]. Other observed lines can be attributed to the following vibration modes: 98 cm^{-1} (F_g), 119 cm^{-1} (F_g), 346 cm^{-1} ($F_g + E_g$), 452 cm^{-1} ($F_g + E_g$), and 611 cm^{-1} ($F_g + A_g$) [21,22]. In our previous manuscript was found out that the line situated at the spectral region 470–570 cm^{-1} could not be Raman lines and most likely correspond to the luminescence of Eu^{3+} ions located at positions with C_{3i} symmetry sites [18]. As it can be seen from Fig. 3b, energy levels of Eu^{3+} ions that occupy C_{3i} site are higher than that for C_2 site [23,24]. So, the energy transfer from C_{3i} to the C_2 site occurs, and the transfer efficiency increases with
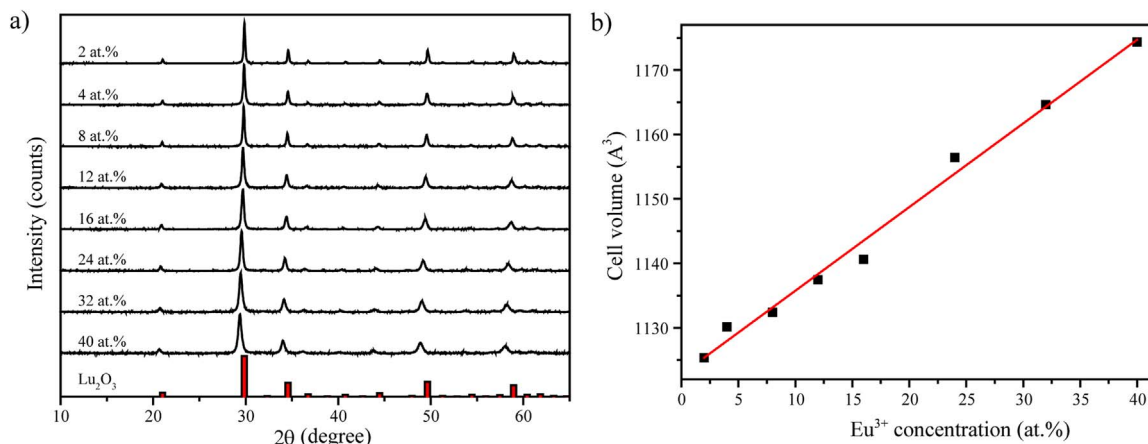

Fig. 1. (a) XRD patterns of Lu_2O_3:Eu^{3+} concentration series and the standard card Lu_2O_3; (b) unit cell volume as a function of Eu^{3+}-doping.