



Investigation of Eu^{3+} luminescence enhancement in LaOF powders codoped with Tb^{3+} and prepared by combustion synthesis



Nikifor Rakov^{a,*}, Simone A. Vieira^a, Renato B. Guimarães^b, Glauco S. Maciel^b

^a PG – Ciência dos Materiais, Universidade Federal do Vale do São Francisco, 48902-300 Juazeiro, BA, Brazil

^b Instituto de Física, Universidade Federal Fluminense, 24210-346 Niterói, RJ, Brazil

ARTICLE INFO

Article history:

Received 30 May 2014

Received in revised form 11 August 2014

Accepted 14 August 2014

Available online 23 August 2014

Keywords:

Rare-earth doped powders

Combustion synthesis

Luminescence spectroscopy

ABSTRACT

Lanthanum oxyfluoride (LaOF) nanocrystalline powders doped with Eu^{3+} , Tb^{3+} and co-doped with both rare-earth elements were prepared by combustion synthesis. Surface morphology and structure of the powders were investigated by scanning electronic microscopy and X-ray powder diffraction. Luminescence experiments were performed with ultraviolet light ($\lambda = 254 \text{ nm}$ and 355 nm). On the basis of the analysis of the luminescence spectra, these powders display the characteristic 4f–4f emissions of Tb^{3+} and Eu^{3+} ions with the most intense emission lines being $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (541 nm) from Tb^{3+} and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (612 nm) from Eu^{3+} . It was observed an enhancement of the red emission at 612 nm from Eu^{3+} ions in co-doped samples. From the analysis of Tb^{3+} emission decay curves it is deduced that Tb^{3+} transfers energy to Eu^{3+} . The energy transfer mechanism was found to be of a resonant type via a dipole–dipole mechanism. The energy transfer efficiency and the critical transfer distance were estimated by the luminescence dynamics analysis.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Inorganic nanostructures doped with trivalent lanthanide ions have been intensively investigated in recent years due to the utility of these materials in numerous important applications such as in medical diagnostics, displays, optoelectronic devices and optical sensors [1–4]. The demand for developing efficient luminescent materials, a suitable host for lanthanide ions, is enormous. It is known that fluoride host matrices have been commonly studied due to their low phonon energy and relatively high chemical stability [4]. Among such materials, lanthanum oxyfluoride (LaOF) has been widely investigated due to offered advantages such as a favorable thermal and chemical stability, and ability to generate strong luminescence in different emission wavelengths for photon conversion [5–9]. In order to improve the luminescence emission of these inorganic nanostructures, which is essential for light manufacturing devices, different interaction mechanisms among rare earth (RE) ions are proposed. For example, energy transfer between Tm^{3+} and Ho^{3+} excited by UV light in LaOF nanocrystals has been investigated and it has been ascribed to a quadrupole–quadrupole mechanism [8]. However, until now no investigation has been performed on the energy transfer mechanisms on LaOF

nanophosphors co-doped with Tb^{3+} and Eu^{3+} ions. The understanding of these mechanisms is important for the use of Eu^{3+} – Tb^{3+} co-doped nanocrystalline powders for white color lighting [8,10] and temperature sensing [11] applications.

Lanthanide-doped LaOF nanostructures have been synthesized by sol–gel techniques, hydrothermal methods, and solid state reactions [6–9,12]. Combustion synthesis is a new method proved to be advantageous because of the fast production of the powder, using a relatively low temperature formation, low cost, and the easy way to achieve high purity and single phase nanomaterials [13]. In the present work, the luminescence properties and energy transfer mechanisms were investigated in Eu^{3+} and Tb^{3+} doped LaOF powders prepared by combustion synthesis for the first time. We found that the dominant energy transfer mechanism between Tb^{3+} and Eu^{3+} in LaOF has a dipole–dipole character.

2. Materials and methods

The powders were synthesized using reagent-grade terbium nitrate, $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, europium nitrate $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich), and lanthanum nitrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich). The fuel used in the process was glycine $\text{C}_2\text{H}_5\text{NO}_2$ (Sigma, 99.5%). To prepare the samples, the metal nitrates and fuel were mixed in a proper molar ratio with de-ionized water forming a solution of 0.11 g/ml that was stirred for 5 min. Then, an aqueous solution (0.025 g/ml) of ammonium fluoride NH_4F (Sigma, p.a.) was added dropwise under constant stirring. Afterward, the mixed solution was kept under constant stirring, at a room temperature, for about 10 min, and a milky solution was finally obtained. Then, the resultant

* Corresponding author.

E-mail address: nikifor.gomez@univasf.edu.br (N. Rakov).

solution, in a porcelain crucible, was placed in a preheated furnace, at 500 °C, for about 15 min, until excess free water evaporated and spontaneous ignition occurred resulting in a fine powder product which was grounded. Finally, the as-prepared powders were sintered at 700 °C for 2 h in an air atmosphere with a heating rate of 100 °C/h and a cooling rate of 100 °C/h. The samples were prepared with the following estimated as-prepared weight (wt%) concentrations of Tb³⁺:Eu³⁺ ions: 1.0:0.0; 0.0:1.0; 1.0:1.0; 2.0:1.0; 3.0:1.0.

The diffractometer used to analyze the crystalline structure of the samples was a Bruker AXS D8 Advance (Cu K α radiation, 40 kV and 40 mA) operating in a Bragg–Brentano θ/θ configuration. X-ray powder diffraction (XRPD) pattern was collected in a flat geometry with steps of 0.02° and accumulation time of 30 s per step. The XRPD data was refined with the Rietveld method using GSAS software [14].

Surface morphology was investigated by scanning electronic microscopy (SEM) using a Hitachi TM-1000 tabletop model coupled with an Oxford Instruments Beryllium-window Energy Dispersive X-ray Spectroscopy (EDXS) detector. The accelerating voltage was preset at 15 kV. Imaging was obtained by a backscattering electron detector with the preset charge-up reduction mode.

Stokes luminescence was obtained using a Xe lamp (500 mW; $\lambda = 254$ nm) and the third-harmonic ($\lambda = 355$ nm) of a Q-switched Nd:YAG laser (5 mJ, 5 ns, 10 Hz) as the excitation sources. The unfocused excitation beam was sent directly to the sample surface and the luminescence emission was collected in a reflection mode at a 45° angle with normal incidence. The spectral data were collected and analyzed by use of a fiber-coupled compact spectrometer (Ocean Optics 2000). Temporal analysis was carried out with the luminescence emission being collected by a fiber probe connected to a spectrograph (Horiba Micro-HR) attached to a photomultiplier tube (Hamamatsu R928). The signal was sent to a fast digital oscilloscope (Tektronix TDS-2000B) for processing. All the experiments were performed at room temperature.

3. Results and discussions

The XRPD pattern of the heat-treated powder co-doped with 1.0 wt% of Tb³⁺ and 1.0 wt% of Eu³⁺ is shown in Fig. 1. The heat-treated sample is fully crystallized with well-defined diffraction peaks and very small background noise. Rietveld refinement was performed in the heat-treated sample and the results are also shown in Fig. 1. The diffraction peaks are identified with two phases: tetragonal LaOF with space group P4/nmm and hexagonal LaF₃ phase with space group P63 cm. The dominant crystalline structure is tetragonal LaOF (card No.: 89-5168) with a phase fraction of ~90%. The calculated LaOF cell parameters are $a = b = 4.097(5)$ Å and $c = 5.834(4)$ Å which are similar to the values found for LaOF nanoparticles [7]. Scherrer's equation was used to estimate the average crystallite size and the result found was ≈ 50.4 nm for LaOF phase using the diffraction peak with $2\theta \approx 26.6^\circ$. XRPD performed on highly doped (above 10 wt%) samples did not show the impurity phase LaF₃ (results not shown here) but energy transfer mechanisms were not studied in those single-phase highly doped samples because the analysis is much more complex due to the presence of additional energy transfer mechanisms such as those involving Eu³⁺–Eu³⁺ and Tb³⁺–Tb³⁺ pairs.

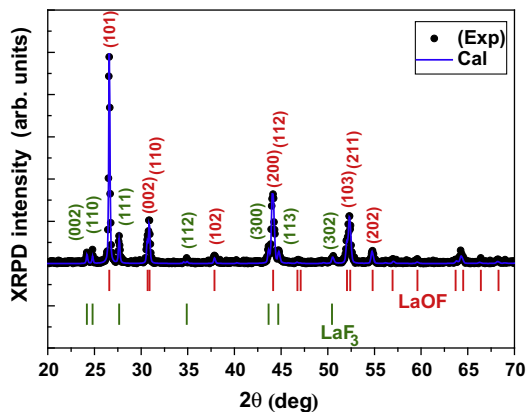


Fig. 1. XRPD experimental data, Rietveld refinement and identified crystalline phases for one of the powder samples (1:1 wt% of Eu³⁺:Tb³⁺) prepared by combustion synthesis.

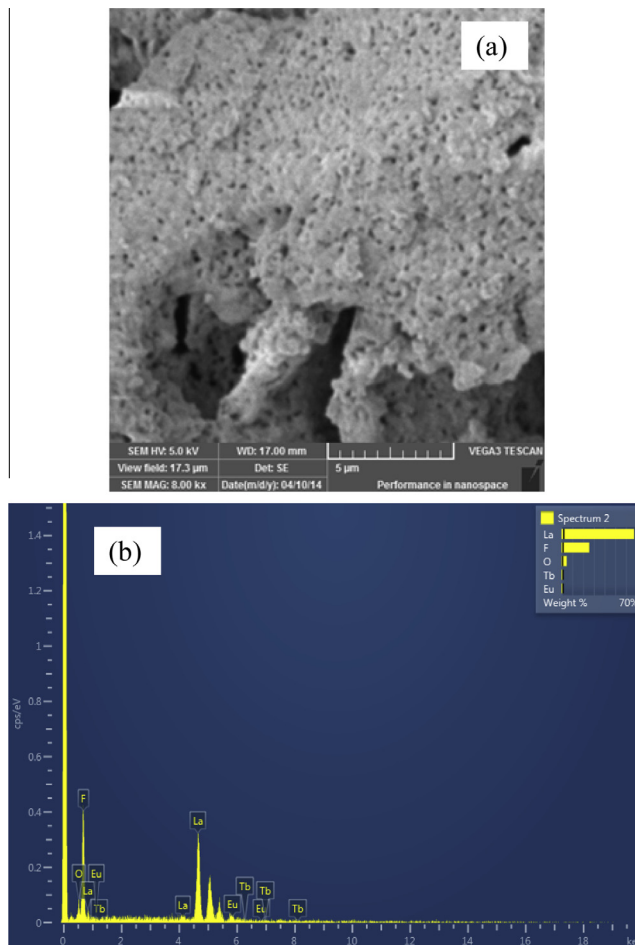


Fig. 2. (a) SEM image (full scale bar is 5 μ m) and (b) EDXS spectrum of one of the powder samples (1:1 wt% of Eu³⁺:Tb³⁺) prepared by combustion synthesis. The inset of the EDXS data shows results of a semi-quantitative view of the elemental composition (in units of weight percent) in the specific inspection field of the SEM image.

Fig. 2 shows (a) the structural analysis of the powder by SEM technique and (b) the elemental analysis/chemical characterization by EDXS. The SEM image shows that the sample is composed of flake-like highly porous particles of various sizes and thicknesses, a consequence of the drastic character of the combustion synthesis reaction. The EDXS data shows that there are representative peaks associated to Tb, Eu, La and F, proving that the doping process was successful. The inset shows results of a semi-quantitative view of the elemental composition (in units of weight percent) in the specific inspection field of the SEM image shown in Fig. 2(a). The areas under selected peaks were used to provide the semi-quantitative elemental composition information. Note that the estimated wt% of Tb and Eu elements (around 1 wt% for each rare-earth element) is similar to the as-prepared values. Light elements such as F and O may show less reliable values. The sample used in Fig. 2 was the one containing 1:1 wt% of Eu³⁺:Tb³⁺ (the same sample that was used to collect the XRPD data shown in Fig. 1).

Fig. 3 shows the Stokes luminescence spectrum of a Tb³⁺ singly doped sample excited at 254 nm. Ligand-to-metal (O²⁻ \rightarrow RE³⁺) charge transfer states and 4f–5d spin allowed transitions are generally responsible for broad optical absorption at this spectral region. However, Ricci and co-workers [15] have ascribed absorption at 250 nm solely to 4f–5d states. It should be noted that under this optical excitation, at $\lambda = 254$ nm, the Tb³⁺ ions are promoted to 4f–5d states and then relax, through nonradiatively mechanisms,

Download English Version:

<https://daneshyari.com/en/article/1610335>

Download Persian Version:

<https://daneshyari.com/article/1610335>

[Daneshyari.com](https://daneshyari.com)