Optical Materials 33 (2010) 119–122

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Energy transfer processes in $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$

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ARTICLE INFO

Article history:
Received 18 May 2010
Received in revised form 12 July 2010
Accepted 13 July 2010
Available online 5 August 2010

Keywords:
Energy transfer
Luminescence
Lanthanide ions

ABSTRACT

The optical spectroscopy and excited state dynamics of the $^5D_3$ and $^5D_4$ levels of Tb^{3+} and $^5D_0$ level of Eu^{3+} have been studied in double phosphate materials having the eulytite disordered cubic structure. In the case of $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$, $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer is observed upon excitation in the Tb^{3+} energy levels located in the UV region. This transfer gives rise to strong emission from the $^5D_0$ level of Eu^{3+}, peaking in the red spectral region at 612 nm. The energy transfer efficiency from the $^5D_4$ level of Tb^{3+} in $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$ has been evaluated and the luminescence quantum yields of $Sr_3Tb(PO_4)_3$ and $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$ have been measured.

1. Introduction

Energy transfer processes involving the Tb^{3+} and Eu^{3+} ions in codoped materials have attracted attention over the years [1–6]. Despite the relative simplicity of the lowest energy level diagrams of the ions, it has been shown that the energy transfer processes can be quite complicated. In a series of recent papers, Mikhailik et al. [7,8] have proposed to use the Tb^{3+} ion as an efficient sensitizer of the red luminescence of Eu^{3+}, by exploiting the strong 4f–5d absorption bands of Tb^{3+} located in the vacuum ultraviolet (VUV), that can be efficiently excited by noble gas discharge. This would be helpful for the development of efficient phosphors for plasma displays and for lighting. In particular, Mikhailik and Kraus have recently shown that efficient $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer occurs in the material $Ba_3Tb_{0.90}Eu_{0.10}(PO_4)_3$ upon VUV excitation [8], but the mechanism and the dynamics of the energy transfer process have not been addressed in detail. For this reason, we have found it interesting to extend their investigation and to provide more insight in the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer process in the similar material $Sr_3Tb_{0.9}Eu_{0.1}(PO_4)_3$.

2. Experimental methods and structural characterization

Polycrystalline samples of $Sr_3Tb(PO_4)_3$, $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$, $Sr_3La_{0.99}Tb_{0.01}(PO_4)_3$ and $Sr_3Y_{0.99}Tb_{0.01}(PO_4)_3$ were obtained by solid state reaction at high temperature (1250 °C, 48 h) starting from $SrCO_3$, $NH_4H_2PO_4$ (both reagent grade), Tb_4O_7 (99.999%), Eu_2O_3 (99.99%), La_2O_3 (99.99%) and Y_2O_3 (99.99%) following the method described in [9].

All the obtained materials are single phase with a eulytite-type structure, as confirmed by powder X-ray diffraction (XRD) measurements, carried out using a Thermo ARL X'TRA powder diffractometer, operating in the Bragg–Brentano geometry and equipped with a Cu-anode X-ray source ($K\alpha_1$, $\lambda = 0.154056$ nm; $K\alpha_2$, $\lambda = 0.154433$ nm; $K\alpha_1/K\alpha_2 = 2$), with a Peltier Si(Li) cooled solid state detector. The XRD patterns were collected with a scan rate of 1.2°/min and an integration time of 1.5 s in the 5–90° 2θ range. The phase identification was performed with the PDF-4 + 2007 database supplied by the International Centre for Diffraction Data (ICDD). Polycrystalline samples were ground in a mortar and then put in a low-background sample holder for the data collection.

Luminescence emission and excitation spectra were measured at room temperature by using a Shimadzu RF-5000 spectrofluorometer equipped with a Xe lamp, using a spectral bandwidth of 1.5 nm. The room temperature decay curves were measured using a Nd-YAG laser as the excitation source. The emitted radiation, collected with a fiber, was measured using a half-meter monochromator, equipped with a 150 lines/mm grating and a GaAs detector. The decay curves were recorded with a 500 MHz digital oscilloscope.

The crystal structures of the eulytite-type materials $Sr_3M(PO_4)_3$ (M = La–Lu, Y) are well known to be cubic (space group number 220) and isomorphous with eulytine mineral ($Bi_4Si_3O_{12}$) [10]. The Sr^{2+}/M^{3+} pairs of cations are disordered on a single crystallographic site whilst the oxygen atoms of the phosphate groups are distributed over three partially occupied sites [9]. The cell parameters do not appear to be significantly affected by the nature of the M^{3+} ion. In fact, $Sr_3Y(PO_4)_3$ (PDF card 00-044-0320), $Sr_3Tb(PO_4)_3$ (PDF card 00-033-1353) and $Sr_3Yb(PO_4)_3$ (PDF card 00-048-0409)

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doi:10.1016/j.optmat.2010.07.008

have almost the same cell volume (1033.29, 1033.06 and 1028.59 Å^3, respectively). The Tb^{3+} and Eu^{3+} dopant ions substitute in the single disordered cationic sites having C_3 point group symmetry.

3. Results and discussion

3.1. Emission and excitation spectra

The emission spectrum of $Sr_3Tb(PO_4)_3$ measured upon excitation at 337 nm (in the $4f^8$ levels of Tb^{3+} located above $^5D_3$) is presented in Fig. 1. The bands are broad due to the presence of disorder in the host, as discussed by Blasse [10]. The spectrum clearly shows strong $^5D_4$ emission and no significant $^5D_3$ emission is observed due to efficient cross relaxation processes of the type

$$^5D_3(Tb^{3+}) + {}^7F_6(Tb^{3+}) \rightarrow {}^5D_4(Tb^{3+}) + {}^7F_0(Tb^{3+})$$

as expected for a fully concentrated Tb^{3+} material [11] or one in which strong clustering is present [12]. Excitation in the UV in the levels above $^5D_3$ is therefore followed by fast non-radiative processes, resulting in the population of the luminescent $^5D_4$ state.

The emission spectrum of $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$ obtained upon excitation at 337 nm (in the Tb^{3+} levels) is also shown in Fig. 1. In this case the spectrum is dominated by strong emission bands from the $^5D_0$ level of Eu^{3+}, as only weak $^5D_4$ emission around 545 nm is observed. The data clearly indicate that $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer occurs.

The excitation spectra of $Sr_3Tb(PO_4)_3$ and $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$ are shown in Fig. 2. In the case of the former compounds, the excitation profile of the $^5D_4$ emission is composed of transitions to $4f^8$ levels of Tb^{3+}. Deep UV bands are not detected with the correct intensity due to the use of a Xe lamp, whose output extends from 200/250 to 800 nm. As for $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$, the excitation spectrum of the Eu^{3+} $^5D_0$ emission is dominated by Tb^{3+} bands extending in the UV region. Only a few Eu^{3+} excitation bands are observed (marked by a star in Fig. 2). These results confirm the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer.Various $Tb^{3+} \rightarrow Eu^{3+}$ phonon assisted energy transfer processes have been proposed in the literature [1–6]; some of the most important are:

$$Tb^{3+}(^5D_4) + Eu^{3+}(^7F_0) + \Delta E_{ph} \rightarrow Tb^{3+}(^7F_4) + Eu^{3+}(^5D_0)$$

$$Tb^{3+}(^5D_3) + Eu^{3+}(^7F_0) \rightarrow Tb^{3+}(^7F_3) + Eu^{3+}(^5D_2) + \Delta E_{ph}$$

where the phonon energies involved (ΔE_{ph}) are relatively low (less than 500 cm^{-1}). Due to fast multiphonon relaxation in the phosphate host, having high energy vibrations in the region of 1000–1100 cm^{-1} [13], energy transfer will lead in all cases only to emission from $^5D_0$.

It is interesting to note that for $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$ the relative intensity of the Eu^{3+} $^5D_0$ emission bands, with respect to the Tb^{3+} $^5D_4$ ones, depends on the excitation pathway. The spectra shown in Fig. 3 are normalized with respect to the peak of the $^5D_4 \rightarrow {}^7F_5$ band of Tb^{3+} around 542 nm. Inspection of the figure shows that upon $^5D_3$ excitation at 377 nm, the Eu^{3+} emission intensity in the 570–700 nm range is 1.22 times stronger than upon $^5D_4$ excitation at 487 nm. This could be due to partial direct excitation of the Eu^{3+} ion at 377 nm (26,525 cm^{-1}) in the $^5G_2$ and $^5G_3$ levels, whose centres of gravity lie in LaF_3 at 26,392 and 26,622 cm^{-1}, respectively [14].

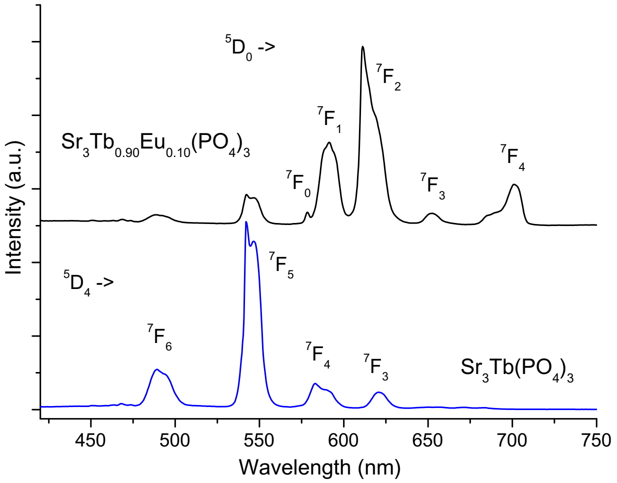

Fig. 1. Room temperature emission spectrum of $Sr_3Tb(PO_4)_3$ and $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$ upon excitation at 337 nm.

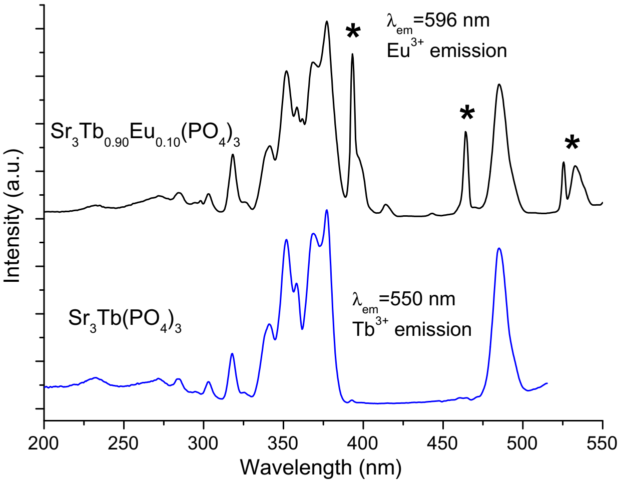

Fig. 2. Room temperature excitation spectra of $Sr_3Tb(PO_4)_3$ and $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$ with emission wavelengths of 550 and 596 nm, respectively. The bands marked with a star are Eu^{3+} excitation bands.

3.2. Excited state dynamics

Decay curves of the $^5D_3(Tb^{3+})$, $^5D_4(Tb^{3+})$ and $^5D_0(Eu^{3+})$ emission were measured at RT upon pulsed laser excitation at 355 nm in the

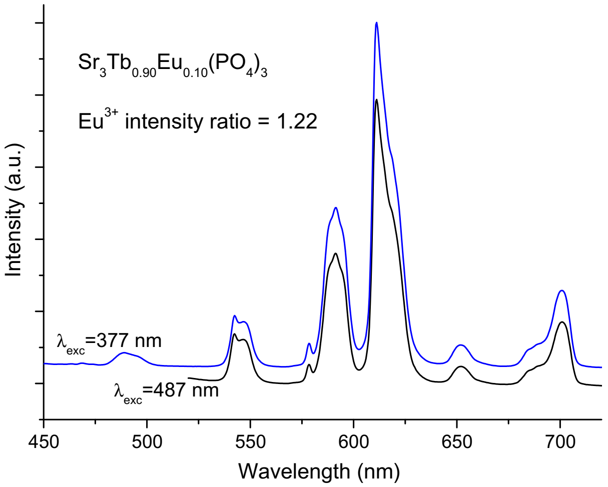

Fig. 3. Room temperature emission spectra of $Sr_3Tb_{0.90}Eu_{0.10}(PO_4)_3$ upon excitation at 377 (top) and 487 nm (bottom). The spectra are normalized for the intensity of the $^5D_4 \rightarrow {}^7F_5$ band at 542 nm.