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Excited state dynamics and energy transfer rates in Sr₃Tb_{0.90}Eu_{0.10}(PO₄)₃

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ABSTRACT

The emission spectrum of neat $Sr_3Tb(PO_4)_3$ upon excitation at 337 nm in the levels above 5D_3 is dominated by 5D_4 emission and no significant emission from 5D_3 is observed due to efficient cross relaxation involving the Tb^{3+} levels. On the other hand, the emission spectrum of the same host containing 10 mol% Eu³⁺ upon excitation at the same wavelength (in the Tb^{3+} levels) is dominated by strong emission bands from the 5D_0 level of Eu³⁺. This clearly indicates that $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer is present. The excitation spectrum of the Eu³⁺ 5D_0 emission is dominated by Tb^{3+} bands extending in the UV region.

The presence of 10 mol% Eu^{3+} in $Sr_3Tb(PO_4)_3$ very strongly shortens the 5D_4 decay time. The decay curve is not far from exponential, indicating that the energy transfer to Eu^{3+} is accompanied by fast energy migration. The transfer regimes are identified and the donor-donor and donor-acceptor transfer microparameters are quantified under the assumption of electric dipole–electric dipole interactions. © 2011 Elsevier B.V. All rights reserved.

1. Introduction

Mikhailik et al. have recently reported on the Tb^{3+} ion acting as an efficient sensitizer of the red ${}^{5}D_{0}$ luminescence of Eu^{3+} , through the strong absorption bands of Tb^{3+} located in the vacuum ultraviolet (VUV), which can be efficiently excited by noble gas discharge. This could give rise to the development of innovative phosphors for plasma displays and lighting. In particular, they have evidenced $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer processes in the hosts $K_{3}Tb(PO_{4})_{2}$, $Ba_{3}Tb(PO_{4})_{3}$, and $TbMgB_{5}O_{10}$ [1–4]. These investigations have motivated us to investigate in detail these processes in the related eulytite host $Sr_{3}Tb_{0.90}Eu_{0.10}(PO_{4})_{3}$ using conventional spectroscopy in the UV–VIS region [5]. In this paper we report in more detail on the excited state dynamics of the ${}^{5}D_{0}(Eu^{3+})$ and ${}^{5}D_{4}(Tb^{3+})$ levels, discuss the transfer regimes in which the transfer processes occur, and quantify the transfer microparameters.

2. Experimental and structural details

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 SrCO₃, NH₄H₂PO₄ (both reagent grade), Tb₄O₇ (99.999%), Eu_2O_3 (99.99%), La_2O_3 (99.99%), and Y_2O_3 (99.99%) following the method described in [6].

All the obtained materials are single phase with a eulytite-type structure, as confirmed by powder X-ray diffraction (XRD) measurements [5]. Luminescence emission and excitation spectra and decay curves were measured at room temperature as described in ref. [5]. 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 (Bi₄Si₃O₁₂)[6]. The Sr^{2+}/M^{3+} pairs of cations are disordered on a single crystal-lographic site of point symmetry C₃ while the oxygen atoms of the phosphate groups are distributed over three partially occupied sites [6].

3. Results and discussion

The room temperature decay curves of the ${}^{5}D_{4}$ level of Tb^{3+} , upon excitation in the levels lying above ${}^{5}D_{3}$, are almost exponential for $Sr_{3}Tb(PO_{4})_{3}$, and show a rise followed by an exponential decay for $Sr_{3}La_{0.99}Tb_{0.01}(PO_{4})_{3}$ and $Sr_{3}Y_{0.99}Tb_{0.01}(PO_{4})_{3}$ [5]. This behavior is due to the slow ${}^{5}D_{3}$ - ${}^{5}D_{4}$ multiphonon relaxation in the diluted samples, while cross relaxation makes this process very fast in $Sr_{3}Tb(PO_{4})_{3}$. The 1/e decay time for the concentrated material is 2.68 ms, i.e. shorter than for the doped materials (3.11 ms for the strontium lanthanum eulytite and 2.98 ms for the strontium yttrium one). This shortening indicates the presence of energy migration in the ${}^{5}D_{4}$ levels, followed by transfer to killer impurities.

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The migration is due to the non-radiative energy transfer process [7,8]:

$${}^{5}D_{4}(Tb^{3+}) + {}^{7}F_{6}(Tb^{3+}) \rightarrow {}^{7}F_{6}(Tb^{3+}) + {}^{5}D_{4}(Tb^{3+})$$

The critical distance R_c of the ${}^5D_4 - {}^5D_4$ energy transfer (assumed to be due to an electric dipole–electric dipole interaction) was evaluated using the equation [9]

$$R_c^6 = 3 \times 10^{12} Q_d \int \frac{f_S(E) F_A(E)}{E^4} dE$$

where Q_d is the oscillator strength of the involved electric dipole absorption transition, $f_S(E)$ represents the normalized emission line shape function of the sensitizer, $F_A(E)$ is the normalized absorption line shape function of the activator, and E is the energy (eV). The calculation was performed assuming $Q_d = 3.0 \times 10^{-7}$ as the oscillator strength of the ${}^7F_6 \rightarrow {}^5D_4$ absorption transition [10]. The overlap between the absorption and emission ${}^7F_6 \leftrightarrow {}^5D_4$ transitions is shown in Fig. 1.

The value $R_c \approx 7.6$ Å is estimated, which can be compared with the minimum Tb–Tb distance of about 4 Å in Sr₃Tb(PO₄)₃; for this reason fast energy migration is predicted to be present in the ⁵D₄ level in this material. We note that at this crystallographic distance, even exchange interaction could be possibly operative [11]. This exploratory estimation of the critical distance is only approximate, due to the several assumptions carried out in the calculation.

In the case of Sr₃Tb_{0.90}Eu_{0.10}(PO₄)₃, the room temperature ⁵D₄ decay curve is not perfectly exponential (Fig. 2) and the decay is much faster than for the materials that do not contain Eu³⁺, with an 1/e decay time of 0.20 ms. Clearly, the Tb³⁺–Eu³⁺ energy transfer is accompanied by fast migration in the Tb^{3+ 5}D₄ subset [5].

The decay curve of ${}^{5}D_{4}$ in $Sr_{3}Tb_{0.90}Eu_{0.10}(PO_{4})_{3}$ (Fig. 3) can be fitted using the Burshtein model, proposed for a donor–acceptor electric dipole–electric dipole transfer in the presence of migration [12,13]

$$I(t) = I_0 \exp\left(-\frac{t}{\tau_0} - \gamma \sqrt{t} - Wt\right)$$

where γ is related to the Tb³⁺ \rightarrow Eu³⁺ energy transfer and *W* is the migration parameter. Assuming a decay time for the isolated donor τ_0 =3.0 ms (compatible with the values for Sr₃La_{0.99}Tb_{0.01}(PO₄)₃



Fig. 1. Emission spectrum of $Sr_3Tb(PO_4)_3$ excited at 337 nm and excitation spectrum observed at 550 nm. The two spectra are vertically displaced for the sake of clarity.



Fig. 2. Spectral overlap of the normalized ${}^7\text{F}_6-{}^5\text{D}_4$ emission and excitation lineshapes.



Fig. 3. Room temperature decay curve of ${}^{5}D_{4}$ in $Sr_{3}Tb_{0.90}Eu_{0.10}(PO_{4})_{3}$ upon pulsed excitation at 355 nm. The solid line represents the fit according to the Burshtein model.

and Sr₃Y_{0.99}Tb_{0.01}(PO₄)₃), we obtain W=3.3 × 10³ s⁻¹ and γ =0.63 ms^{-1/2}. Since [13]

$$\gamma = \frac{4}{3}\pi^{3/2} N_{Eu} C_{TbEu}^{1/2}$$

where N_{Eu} is the acceptor concentration (ions/cm³) and C_{TbEu} is the donor–acceptor transfer microparameter. We obtain $C_{TbEu}=4.8 \times 10^{-41} \text{ cm}^6/\text{s}$ and, from this value, $R_c=7.1 \text{ Å}$ is estimated for the Tb³⁺ \rightarrow Eu³⁺ energy transfer from ⁵D₄. The assumption of an electric dipole–electric dipole mechanism is reasonable in a low symmetry geometry (C₃) for Tb³⁺ and Eu³⁺ [14], even though the exchange interaction cannot be completely ruled out [11].

Moreover, in the case of an electric dipole–electric dipole interaction *W* is given by [15]

$$W = \pi \left(\frac{2\pi}{3}\right)^{3/2} N_{Tb} N_{Eu} C_{TbTb}^{1/2} C_{TbEu}^{1/2}$$

where N_{Tb} is the donor concentration (ions/cm³) and C_{TbTb} is the donor–donor transfer microparameter. From the value of W and the energy transfer microparameter C_{TbEu} , it is possible to evaluate the value of the donor–donor microparameter C_{TbTb} (3.0 × 10^{-40} cm⁶/s) and therefore the critical distance for the Tb³⁺– Tb³⁺ electric dipole–electric dipole transfer, R_c =9.8 Å, higher than

the approximate value estimated above from the spectral overlap of the donor absorption and emission transitions (Fig. 2).

The donor-donor transfer appears to be significantly faster than the donor-acceptor one, in agreement with the Burshtein model describing a regime in which the donor-donor microparameter is larger than the donor-acceptor one [16]. In the present case, the values obtained in the frame of the Burshtein (hopping) model are comparable to the ones found by Kim Anh et al. $(C_{TbTb}=5.7 \times 10^{-40} \text{ cm}^6/\text{s}, C_{TbEu}=2.0 \times 10^{-41} \text{ cm}^6/\text{s})$ for the Tb³⁺-Eu³⁺ energy transfer in Y₂O₃ crystals [17].

4. Conclusions

In this work, we have investigated the excited state dynamics of Tb³⁺ and Eu³⁺ in several eulytite double phosphates, concentrating our attention on Sr₃Tb(PO₄)₃ and Sr₃Tb_{0.90}Eu_{0.10}(PO₄)₃. The energy migration in the ⁵D₄ subset of Tb³⁺ ions appears to occur in the hopping regime and is faster than the energy transfer from ⁵D₄ to the energy levels of Eu³⁺. The transfer microparameters for the electric dipole–electric dipole interaction are comparable to the ones obtained for the same transfer in Y₂O₃ crystals. The fast migration among the Tb³⁺ ions greatly enhances the transfer probability, despite the relatively low rate of the Tb³⁺–Eu³⁺ transfer process.

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