

# Optical properties of $Tb^{3+}$ in the diphosphate $CsY_{1-x}Tb_xP_2O_7$

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## Abstract

The luminescence of  $Tb^{3+}$  ion in the diphosphate  $CsY_{1-x}Tb_xP_2O_7$  ( $0 < x \leq 1$ ) is reported. A high concentration quenching of the emission from the  $^5D_3$  level due to a  $^5D_3 \rightarrow ^5D_4$  cross-relaxation process is pointed out, well described by the Inokuti and Hirayama model in the case of a dipole–dipole interaction. On the other hand, a weak concentration quenching of the emission originating from the  $^5D_4$  level is observed. The luminescence dynamics showed that a fast diffusion occurs for the high  $Tb^{3+}$  ion concentration, involving the  $^5D_4$  level; this process is moreover phonon-assisted.

## 1. Introduction

Some concentrated phosphates like  $NdP_5O_{14}$  [1] are known as laser materials; moreover, they show a very weak concentration luminescence quenching. These good optical properties have to be partly related to their crystallographic characteristics. There is a weak interaction between the lanthanide ions, due to the fact that Nd polyhedra are separated from each other by phosphate groups, leading to a minimum Nd–Nd distance of 5.20 Å in  $NdP_5O_{14}$  [2]. The diphosphates  $RbYP_2O_7$  and  $CsYP_2O_7$  present similar crystallographic features. Refinement of the  $RbYP_2O_7$  structure has led to a minimum Y–Y distance equal to 5.30 Å [3]. The optical properties of these materials were thus investigated in our laboratory, especially when doped with  $Tb^{3+}$  or  $Eu^{3+}$  ions.

Since optical similarities between  $RbYP_2O_7:Tb^{3+}$  and  $CsYP_2O_7:Tb^{3+}$  are observed, we only report the results concerning the caesium compound in this paper. The influence of  $Tb^{3+}$  concentration on the luminescence from the  $^5D_3$  and  $^5D_4$  levels is analyzed. The luminescence dynamics allow us to explain the processes involved in the quenching of emission originating from  $^5D_3$  and  $^5D_4$  levels.

## 2. Experimental details

The diphosphates  $CsY_{1-x}Tb_xP_2O_7$  ( $0 < x \leq 1$ ) were synthesized in the solid state by weighing out stoichiometric amounts of  $Cs_2CO_3$  (STREM, 99%),  $Y_2O_3$  (STREM, 99.9%),  $TbPO_4$  and  $(NH_4)_2HPO_4$  (STREM); the preliminary synthesis of  $TbPO_4$  was described else-

where [4]. The mixtures were put in an alumina crucible and heated at 600 °C for 4 h and then at 700–800 °C for 16 h.

The apparatus for optical measurements is presented in ref. 4.

## 3. Optical results

The emission spectra of  $CsY_{1-x}Tb_xP_2O_7$  ( $0 < x \leq 1$ ) were recorded at 300 and 77 K, under excitation at 337.1 nm. Figure 1 shows the spectrum recorded at 77 K for  $CsY_{0.98}Tb_{0.02}P_2O_7$  in which the  $^5D_3 \rightarrow ^7F_J$  (370–480 nm) and  $^5D_4 \rightarrow ^7F_J$  (480–680 nm) emissions are observed ( $0 \leq J \leq 6$ ). The  $^5D_3 \rightarrow ^7F_J$  emission shows a maximum intensity at a concentration of about 2% ( $x \approx 0.02$ ) then decreases quickly and is quenched above 10% ( $x \approx 0.1$ ), whereas the  $^5D_4 \rightarrow ^7F_J$  luminescence intensity increases rapidly; the maximum is obtained for a concentration of about 50% ( $x \approx 0.5$ ). A weak concentration quenching is noticed beyond this value (Fig. 2). The ratio of  $^5D_3$  and  $^5D_4$  emission intensities is temperature independent. The luminescence decay times of the  $^5D_3 \rightarrow ^7F_4$  emission ( $\lambda = 435.6$  nm) were recorded at 300 and 77 K under excitation at 337.1 nm. For a very low concentration (less than 0.5%) the decay is exponential with a time constant of about 2 ms. When the concentration is increased, the initial part of the curves becomes non-exponential and the time constants decrease rapidly ( $\tau = 0.6$  ms for  $x = 0.06$ ). Figure 3 shows the decay profiles obtained for some  $Tb^{3+}$  concentrations, at 300 K. Temperature has no influence on the decay curves.

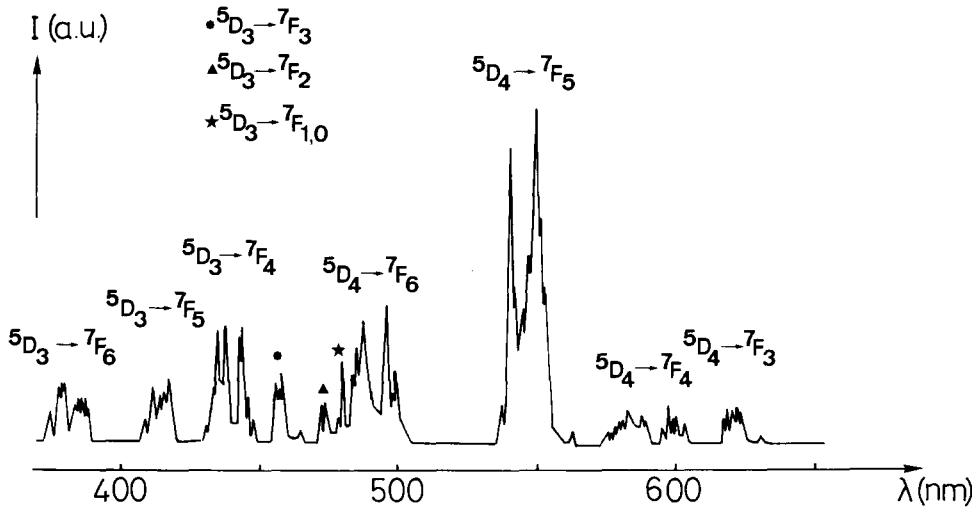


Fig. 1. Emission spectrum of  $Tb^{3+}$  in  $CsY_{0.98}Tb_{0.02}P_2O_7$  at 77 K ( $\lambda_{exc} = 337.1$  nm).

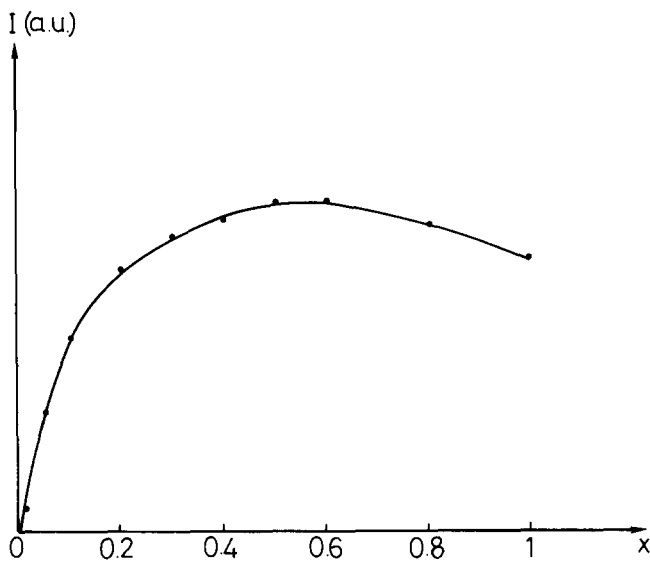


Fig. 2. Variation of the  ${}^5D_4 \rightarrow {}^7F_5$  luminescence intensity versus the  $Tb^{3+}$  ion content ( $\lambda_{exc} = 337.1$  nm).

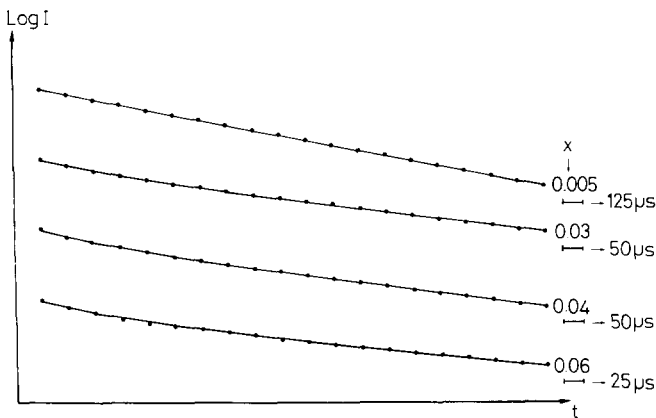


Fig. 3.  ${}^5D_3 \rightarrow {}^7F_4$  luminescence decay curves versus the  $Tb^{3+}$  ion concentration at 300 K ( $\lambda_{exc} = 337.1$  nm). ●, experimental points; —, fitting by the relation (2).

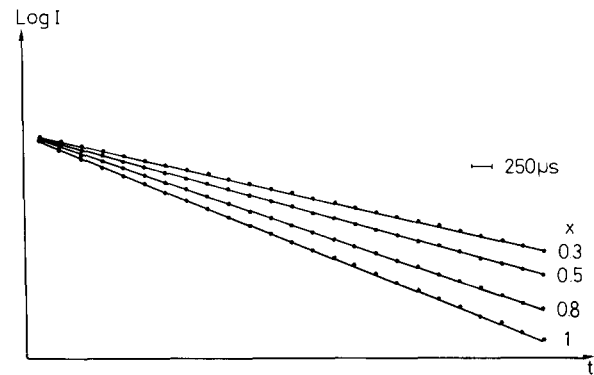


Fig. 4.  ${}^5D_4 \rightarrow {}^7F_5$  luminescence decay curves versus the  $Tb^{3+}$  ion concentration at 300 K ( $\lambda_{exc} = 337.1$  nm). ●, experimental points; —, fitting by an exponential.

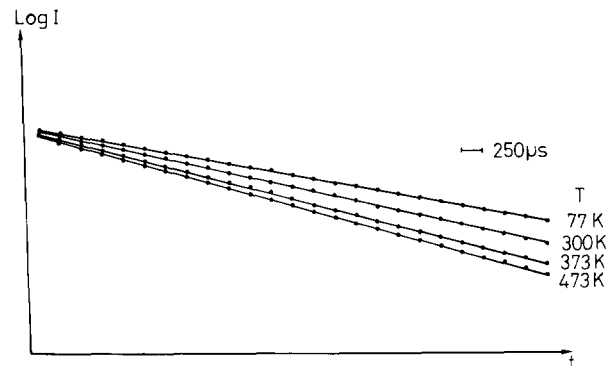


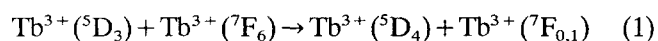
Fig. 5.  ${}^5D_4 \rightarrow {}^7F_5$  luminescence decay curves versus the temperature for the compound  $CsY_{0.8}Tb_{0.2}P_2O_7$  ( $\lambda_{exc} = 337.1$  nm). ●, experimental points; —, fitting by an exponential.

With the same excitation conditions, luminescence decays of  ${}^5D_4 \rightarrow {}^7F_5$  emission ( $\lambda = 550.0$  nm) were achieved. For a  $Tb^{3+}$  content below 10%, the decays exhibit an initial rise which is a consequence of relaxation from  ${}^5D_3$  to  ${}^5D_4$ . The time constants do not vary with the active ion content below 30% (the average value is 4.1 ms at 300 K and 4.9 ms at 77 K). For  $0.3 \leq x \leq 1$ ,

the time constants decrease; the value obtained for  $x=1$  is 2.3 ms at 300 K and 2.9 ms at 77 K. Figure 4 shows decay curves recorded for some Tb<sup>3+</sup> concentrations, at 300 K. The decays are perfectly exponential in the whole concentration range ( $0 < x \leq 1$ ) and are influenced by temperature: the time constant values decrease when temperature is increased ( $\tau=5.0$  ms at 77 K and 3.3 ms at 473 K for  $x=0.2$ , for instance) (Fig. 5).

#### 4. Discussion

A cross-relaxation process has been put forward to explain the concentration quenching of the <sup>5</sup>D<sub>3</sub> emission of Tb<sup>3+</sup> in different compounds [4]. It occurs because of the quasi-resonance of the energy gaps <sup>5</sup>D<sub>3</sub>-<sup>5</sup>D<sub>4</sub> and <sup>7</sup>F<sub>6</sub>-<sup>7</sup>F<sub>0,1</sub> according to:



and leads to a non-exponential part of the decay curves. In order to determine the interactions responsible for the non-radiative relaxation from the <sup>5</sup>D<sub>3</sub> level, the luminescence decays of <sup>5</sup>D<sub>3</sub> → <sup>7</sup>F<sub>4</sub> emission were fitted using the Inokuti and Hirayama model, corresponding to a direct transfer without diffusion. The intensity  $I(t)$  of the <sup>5</sup>D<sub>3</sub> emission is given by [5]:

$$I(t) = I(0) \exp[-t/\tau_0 - I(1-3/n)C/C_0(t/\tau_0)^{3/n}] \quad (2)$$

in which  $I(0)$  is the intensity at  $t=0$ ,  $\tau_0$  is the radiative lifetime of the <sup>5</sup>D<sub>3</sub> level, without transfer,  $C$  is the Tb<sup>3+</sup> concentration (at.%),  $C_0$  is the transfer critical concentration,  $n=6, 8, 10$ , respectively, for electric dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions;  $I(1-3/n)$  is the Euler function whose values are 1.77, 1.43 and 1.3 for  $n=6, 8, 10$ , respectively.

The best results are obtained with  $n=6$ , corresponding to a dipole-dipole interaction (Fig. 3), using for  $\tau_0$  the time constant measured for CsY<sub>0.995</sub>Tb<sub>0.005</sub>P<sub>2</sub>O<sub>7</sub>, i.e. 2.2 ms at 300 K and 2.1 ms at 77 K. From the theoretical fit, the critical concentration was calculated: its value is  $C_0=5\%$  ( $x=0.05$ ). Using the following relation [6]:

$$R_0 = 2(3/4\pi N_0)^{1/3} \quad (3)$$

where  $N_0$  is the critical concentration expressed as a number of Tb<sup>3+</sup> ions per cm<sup>3</sup>, we find a transfer critical distance  $R_0$  of about 19 Å. Furthermore, a <sup>5</sup>D<sub>3</sub> → <sup>5</sup>D<sub>4</sub> multiphonon relaxation process is negligible in our materials.

From the decays of the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> emission, we can note that, for  $0 < x \leq 0.3$ , the active ions act as isolated ones. Above this concentration, the decay curves remain exponential and the time constant values decrease strongly; this means that we are probably dealing with a fast diffusion process. This behaviour has been studied for rare earth ions in crystals by Gandrud *et al.* [7]. This rapid energy migration through Tb<sup>3+</sup> ions is phonon-assisted because of its strong dependence on temperature (Fig. 5). The pentaphosphate NdP<sub>5</sub>O<sub>14</sub> also presents similar optical characteristics [8]. In spite of this fast diffusion, a weak concentration quenching is observed, due to the relatively long distance between Tb<sup>3+</sup> ions in CsYP<sub>2</sub>O<sub>7</sub>:Tb<sup>3+</sup>; the minimum Tb-Tb distance is about 5.40 Å in CsTbP<sub>2</sub>O<sub>7</sub>. Another possible reason for the weak quenching could be a small number of acceptors/traps and/or a weak donor-acceptor interaction.

#### 5. Conclusion

A cross-relaxation process has been observed in CsY<sub>1-x</sub>Tb<sub>x</sub>P<sub>2</sub>O<sub>7</sub>; it is responsible for the non-radiative de-excitation from <sup>5</sup>D<sub>3</sub> to <sup>5</sup>D<sub>4</sub>. The <sup>5</sup>D<sub>3</sub> luminescence dynamics is well described by the Inokuti and Hirayama model; a dipole-dipole interaction was determined between the active ions. A fast diffusion process through the <sup>5</sup>D<sub>4</sub> level has been pointed out; it is a function of temperature. Nevertheless, a weak concentration quenching has been noted for the <sup>5</sup>D<sub>4</sub> emission.

The optical study of the Eu<sup>3+</sup> photoluminescence in CsYP<sub>2</sub>O<sub>7</sub> is in progress in our laboratory. The fluorescence intensity of this ion could subsequently be optimized by means of a Tb<sup>3+</sup> → Eu<sup>3+</sup> energy transfer.

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