

Optical spectroscopy of zinc metaphosphate glasses activated by Ce³⁺ and Tb³⁺ ions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 3499

(<http://iopscience.iop.org/0953-8984/18/13/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 09:18

Please note that [terms and conditions apply](#).

Optical spectroscopy of zinc metaphosphate glasses activated by Ce³⁺ and Tb³⁺ ions

U Caldiño¹, A Speghini² and M Bettinelli²

¹ Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, PO Box 55-534, 09340 México, DF, Mexico

² Dipartimento Scientifico e Tecnologico, Università di Verona, and INSTM, UdR Verona, Strada Le Grazie 15, I-37314 Verona, Italy

E-mail: cald@xanum.uam.mx

Received 26 December 2005, in final form 14 February 2006

Published 17 March 2006

Online at stacks.iop.org/JPhysCM/18/3499

Abstract

The photoluminescence of Ce³⁺ and Tb³⁺ ions in zinc metaphosphate glasses is investigated. The blue and green emissions of Tb³⁺ ions are enhanced upon UV excitation through energy transfer from Ce³⁺ to Tb³⁺ ions. The efficiency of such an energy transfer was estimated based on spectroscopic data and resulted in being about 20–23%. Spectroscopic data revealed that the energy transfer occurs via a non-radiative process inside Ce³⁺–Tb³⁺ clusters formed in the glass. This ion clustering could be useful for the design of efficient conversion phosphors of ultraviolet to blue and green light.

1. Introduction

The phenomenon of resonant energy transfer among impurity ions in a solid material has been the subject of intense research during recent decades, mainly because of its importance in the development of efficient phosphor materials (such as flat panel displays [1] and radiation detectors [2]), fibre-optic amplifiers (used in communication devices [3–5]), and solid state laser sources, in which the energy transfer processes can cause the reduction of the laser threshold due to an enhancement of the luminescence emission [6, 7].

Broad band emitters are usually used to sensitize the luminescence of rare earth and transition metal ions. In particular, in solids the Ce³⁺ ion shows efficient broad band emission due to its 4f–5d parity allowed electric dipole transition. In co-doped materials the Ce³⁺ ion acts as a good sensitizer, transferring a part of its energy to activator ions such as Eu²⁺ [8], Tb³⁺ [9, 10] and Mn²⁺ [11–13].

Phosphate glasses have attracted renewed interest due to their potential use in several optical devices. Moreover, the phosphate glasses are relatively easy to prepare and show various interesting physical and chemical properties, which make them attractive as hosts for

luminescent ions [14]. In particular, zinc metaphosphate glasses have been used in glass–polymer composites, optical waveguides and solid state laser sources, as well as solders and welds between glassy and metallic parts in electronic circuits and television tubes, due to the fact that their thermal expansion coefficient is similar to that of many metals [15]. Considering the importance of finding efficient luminescent materials for the design of optical devices based on the zinc metaphosphate composition, in the present investigation a spectroscopic study of the sensitizing of the Tb³⁺ blue and green luminescence through Ce³⁺ ions is presented. To our knowledge no work has been reported on the luminescence of this host material co-doped with Ce³⁺ and Tb³⁺ ions. In order to obtain a better understanding of the Ce³⁺ → Tb³⁺ energy transfer, emission, excitation and lifetime data for the singly doped Tb³⁺ zinc metaphosphate glass have also been obtained. Spectroscopic data for the Ce³⁺-activated zinc metaphosphate glass have been previously reported and analysed [16].

2. Experimental details

The molar compositions of the glasses under investigation are Zn(PO₃)₂ 99%–Tb(PO₃)₃ 1% and Zn(PO₃)₂ 98.9%–Ce(PO₃)₃ 0.1%–Tb(PO₃)₃ 1%. The zinc metaphosphate glass singly doped with the same Ce³⁺ concentration (Zn(PO₃)₂ 99.9%–Ce(PO₃)₃ 0.1%) has been previously analysed [16]. The three samples will be referred hereafter as ZPOT, ZPOCT and ZPOC, respectively.

The zinc metaphosphate glasses were prepared by mixing appropriate quantities of ZnO (Aldrich 99+%), NH₄H₂PO₄ (Carlo Erba RPE), Ce(NO₃)₃·6H₂O (Aldrich 99.99%) and Tb₄O₇ (Aldrich 99.99+%) in a sintered alumina crucible, and melting the mixture for 2 h at 1250 °C. The melts were quenched onto a copper plate. The glasses were annealed for 12 h at 350 °C to obtain thermal and structural stability.

Luminescence spectra were recorded by means of a Perkin Elmer LS-50B spectrometer. The decay curve of the Tb³⁺ emissions and time resolved spectra were obtained with this spectrometer operating in the phosphorescence mode. All the luminescence spectra with exception of those corresponding to the Ce³⁺ emission were recorded with a delay time of 0.1 ms after the pulse excitation (0.1 ms width pulses). The decay curve of the Ce³⁺ emission was obtained by exciting at 290 nm with the second harmonic of a dye laser (using Rhodamine 6G as the dye) pumped with the second harmonic (532 nm) of a pulsed Nd-YAG laser. A fibre optic probe was employed to collect the emission. The signal was analysed by means of a half-metre monochromator equipped with a 150 lines mm⁻¹ grating. A GaAs photomultiplier and a digital oscilloscope were used to record the decay curves. The decay times were obtained from the emission decay curves using a deconvolution procedure, which takes into account the shape and duration (about 10 ns) of the excitation pulse.

All measurements were carried out at room temperature.

3. Theoretical considerations

The microscopic mechanisms of energy transfer were first explained by Förster [17], who showed that the energy transfer probability through an electric dipole–dipole (dd) interaction mechanism is proportional to the overlap of the sensitizer emission and activator absorption spectra and to R^{-6} , where R is the distance between the sensitizer and activator ions. Thus, the transfer probability for an electric dd interaction is given by

$$P_{sa}^{dd} = \frac{3\hbar^4 c^4 Q_a}{4\pi n^4 \tau_s^0 R_{sa}^6} \int \frac{f_s(E) F_a(E) dE}{E^4}, \quad (1)$$

where $\int [f_s(E)F_a(E)/E^4] dE$ is the spectral overlap integral between the normalized line-shape functions of the sensitizer emission $f_s(E)$ and activator absorption $F_a(E)$, with E being the average energy of the overlapping transition; n is the refractive index of the host medium, τ_s^0 is the sensitizer intrinsic lifetime in the absence of the activator, and Q_a is the oscillator strength of the activator absorption transition, which is in resonance with the sensitizer emission transition. The remaining symbols in equation (1) have their usual meaning.

It is well known that energy transfer will not be important if the sensitizer to activator separation exceeds the critical separation. In an electric dd interaction process the critical separation R_{sa}^o (dd) is defined as that for which the probability of transfer equals the probability of radiative emission of the sensitizer, that is, $P_{sa}(\text{dd})\tau_s^0 = 1$. Then, from equation (1), R_{sa}^o (dd) is given by

$$R_{sa}^o(\text{dd}) = \left(\frac{3\hbar^4 c^4 Q_a}{4\pi n^4} \int \frac{f_s(E)F_a(E) dE}{E^4} \right)^{1/6}. \quad (2)$$

The classic work of Förster was extended by Dexter [18] to include higher-order multipole interactions. Thus, the transfer probability for an electric dipole–quadrupole (dq) interaction is given by

$$P_{sa}^{\text{dq}} = \frac{3\hbar^4 c^4 f_q \lambda_s^2 Q_a}{4\pi n^4 \tau_s^0 f_d R_{sa}^8} \int \frac{f_s(E)F_a(E) dE}{E^4}, \quad (3)$$

where λ_s is the wavelength position of the sensitizer emission, and f_q and f_d are the oscillator strengths of the activator ion electric quadrupole and dipole transitions, respectively.

The corresponding critical separation R_{sa}^o (dq) for an electric dq interaction process is given by

$$R_{sa}^o(\text{dq}) = \left(\frac{3\hbar^4 c^4 f_q \lambda_s^2 Q_a}{4\pi n^4 f_d} \int \frac{f_s(E)F_a(E) dE}{E^4} \right)^{1/8}. \quad (4)$$

The emission probability of excited ions increases with the non-radiative energy transfer to activator ions:

$$\frac{1}{\tau_s} = \frac{1}{\tau_s^0} + P_{sa}. \quad (5)$$

So that the P_{sa} probability of sensitizer–activator energy transfer can be expressed in terms of decay times [16]:

$$P_{sa} = \frac{1}{\tau_s} - \frac{1}{\tau_s^0}, \quad (6)$$

where τ_s and τ_s^0 are the decay times of the sensitizer in the presence and absence of the activator, respectively.

Taking into account that the efficiency η of energy transfer can be defined as the ratio of the P_{sa} transfer probability to the $1/\tau_s$ sensitizer emission probability [16],

$$\eta = \frac{P_{sa}}{1/\tau_s}, \quad (7)$$

then, from equations (6) and (7), η can be expressed in terms of lifetimes [19]:

$$\eta = 1 - \frac{\tau_s}{\tau_s^0}. \quad (8)$$

The energy transfer efficiency can also be measured from the intensities of the sensitizer emission in the presence (I_s) and absence (I_s^0) of the activator, through the following expression [16]:

$$\eta = 1 - \frac{I_s}{I_s^0}. \quad (9)$$

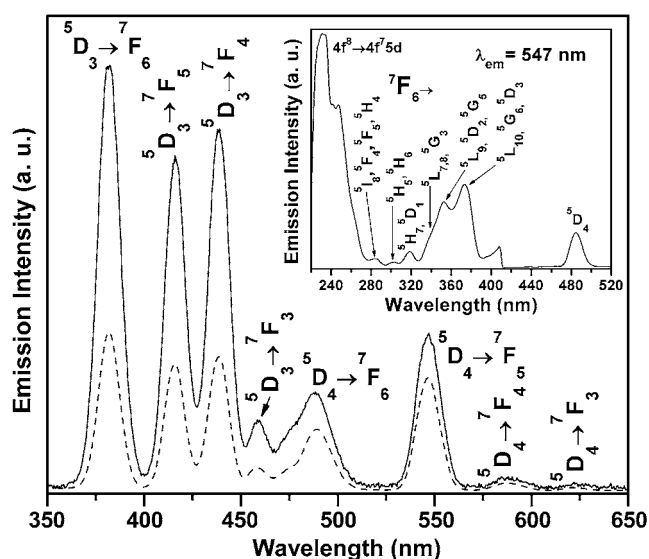


Figure 1. Emission and excitation (inset) spectra of ZPOT. The emission spectrum was obtained after excitation at 232 nm (solid curve) and 352 nm (dashed curve). The excitation spectrum was monitored at 547 nm.

4. Results and discussion

4.1. $Zn(PO_3)_2:Tb^{3+}$

The excitation and emission spectra displayed by the Tb^{3+} singly doped glass (ZPOT) are shown in figure 1. The excitation spectrum (displayed in the inset of figure 1) was monitored at 547 nm, which corresponds to the $^5D_4 \rightarrow ^7F_5$ transition. This spectrum consists of the excitation peaks characteristic of Tb^{3+} ions, which correspond to transitions from the $^7F_6(4f^8)$ ground state to higher energy states of the $4f^8$ and $4f^75d$ configurations. The excitation bands associated with the $4f^8 \rightarrow 4f^75d$ electric dipole allowed transitions, peaking at 232 nm (see the inset of figure 1), appear to be significantly more intense than those associated with the $4f^8 \rightarrow 4f^8$ forbidden transitions. The emission spectra were obtained under excitation into the $4f^8 \rightarrow 4f^75d$ and $4f^8(^7F_6) \rightarrow 4f^8(^5L_9, ^5D_2, ^5G_5)$ absorption bands at 232 and 352 nm, respectively. These spectra consist of several bands associated with $4f^8 \rightarrow 4f^8$ transitions from the 5D_3 (blue emissions) and 5D_4 (green–red emissions) levels to the 7F_6 , 7F_5 , 7F_4 and 7F_3 multiplets. Excitation at 232 nm leads to predominant blue emissions (transitions from the 5D_3 multiplet) relative to the green emissions (transitions from the 5D_4 multiplet). This fact suggests that at 1% concentration of $Tb(PO_3)_3$ there is a very small non-radiative relaxation from the 5D_3 to the 5D_4 level. Such a non-radiative relaxation is promoted by the excitation from the 7F_6 to the 7F_0 level through a cross-relaxation process [20]. It is well known that the energy difference between the 5D_3 and 5D_4 levels is the same as that between the 7F_0 and 7F_6 levels, so the 5D_3 to 7F_j transitions of some materials with high Tb^{3+} concentration are quenched by the energy transfer of identical centres, $^5D_3 + ^7F_6 \rightarrow ^5D_4 + ^7F_0$. Then, only 5D_4 to 7F_j emissions are observed. Excitation at 352 nm gives rise to weaker blue emissions, so they are closely comparable to the green emissions. Therefore, the relative emission intensities in the blue and the green depends on the excitation into the fd or f states, as probably the pathways populating the emitting states are different in the two cases.

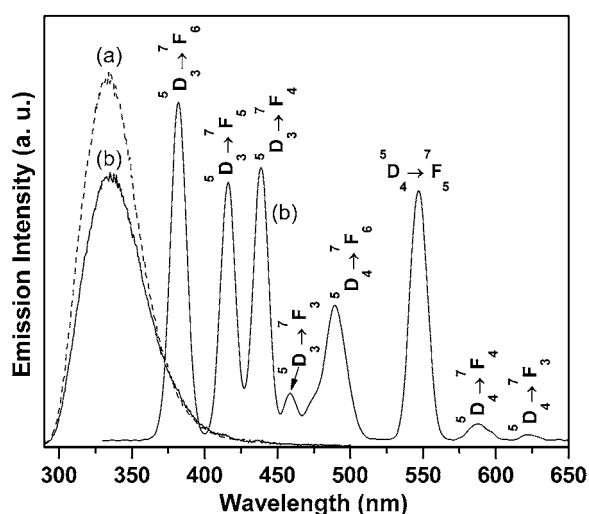


Figure 2. Emission spectra after 294 nm excitation of (a) ZPOC (dashed curve) [16] and (b) ZPOCT (solid curve).

Table 1. Decay times of the 5d state of Ce³⁺ and the ⁵D₃ and ⁵D₄ states of Tb³⁺.

Glass	λ_{exc} (nm)	Level	τ_{Ce} (ns)	τ_{Tb} (ms)
ZPOC	290	5d	26 ± 1 [16]	
ZPOT	352	⁵ D ₃		0.9 ± 0.1
		⁵ D ₄		3.3 ± 0.2
ZPOCT	290	5d	20 ± 1	
		⁵ D ₃		0.8 ± 0.1
		⁵ D ₄		3.2 ± 0.2
	352	⁵ D ₃		0.9 ± 0.1
		⁵ D ₄		3.2 ± 0.2

Lifetime measurements of the ⁵D₃ and ⁵D₄ levels of Tb³⁺, monitoring the blue ⁵D₃ → ⁷F_{6,5,4} and green ⁵D₄ → ⁷F_{6,5} emission transitions, respectively, were carried out at an excitation wavelength of 352 nm. The Tb³⁺ emission decays were found to be described by a single-exponential decay curve, and lifetime values of ~0.9 and ~3.3 ms were obtained for the ⁵D₃ and ⁵D₄ levels, respectively (see table 1).

4.2. Zn(PO₃)₂:Ce³⁺:Tb³⁺

The emission spectrum of the zinc metaphosphate glass doped with Ce³⁺ and Tb³⁺ ions (ZPOCT) when excitation is carried out with 294 nm radiation lying within the 4f → 5d absorption band of Ce³⁺ ions is portrayed in figure 2 (solid curve). The spectrum consists of the 5d → 4f ultraviolet emission broad band assigned to Ce³⁺ ions and the blue (⁵D₃ → ⁷F_{6,5,4,3}) and green–red (⁵D₄ → ⁷F_{6,5,4,3}) emissions corresponding to Tb³⁺ ions.

The 5d–4f electric dipole allowed transitions of Ce³⁺ are several orders of magnitude stronger than the 4f intraconfigurational transitions of Tb³⁺, so Ce³⁺ can strongly absorb UV radiation and transfer a part of its energy to Tb³⁺. Such an energy transfer induces an enhancement of the Tb³⁺ emissions after Ce³⁺ excitation. This fact can be visualized in figure 3, which shows the emission spectra of ZPOCT excited at 294 nm (within the 4f → 5d

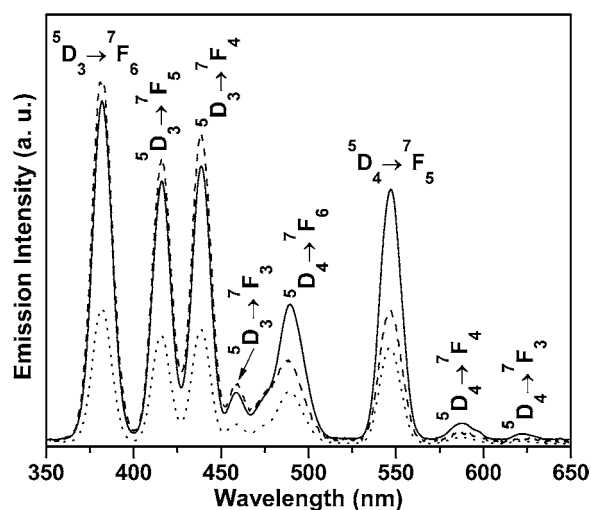


Figure 3. Emission spectra of ZPOCT excited at 294 nm (solid curve), 232 nm (dashed curve) and 352 nm (dotted curve).

absorption band of Ce^{3+} ions), 232 nm (inside the $4f^8 \rightarrow 4f^75d$ transitions of Tb^{3+} ions) and 352 nm (within the ${}^7F_6 \rightarrow {}^5L_9$, 5D_2 , 5G_5 transitions of Tb^{3+}). The blue emissions from the 5D_3 level after Ce^{3+} excitation at 294 nm are enhanced 2.6 times relative to those recorded with excitation at 352 nm, and the green emissions from the 5D_4 level after 294 nm excitation are enhanced 1.8 and 2.6 times when compared to those obtained with excitation at 232 and 352 nm, respectively.

The emission spectrum corresponding to the singly doped glass with the same concentration of Ce^{3+} (ZPOC) [16], measured in the same experimental conditions, is also shown in figure 2 (dashed curve) for comparison. It is clear that the addition of Tb^{3+} ions in the Ce^{3+} doped glass causes a decrease of the overall emission of Ce^{3+} ions, which implies that the Ce^{3+} transfers a part of its energy before it can fluoresce. This fact and that Tb^{3+} ions cannot be directly excited at 294 nm (see the inset of figure 1) suggest that the $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer takes place through a non-radiative process.

Figure 4 shows the excitation spectra of ZPOT (dashed curve) and ZPOCT (solid curve). The excitation spectra were monitored at 547 nm, inside the ${}^5D_4 \rightarrow {}^7F_5$ emission band of Tb^{3+} . The excitation spectrum displayed by the co-doped glass presents, in addition to the $4f^8 \rightarrow 4f^8$ and $4f^8 \rightarrow 4f^75d$ absorption transitions of Tb^{3+} , a broad band similar to the $4f \rightarrow 5d$ Ce^{3+} absorption band observed in the ZPOC excitation spectrum [16] (see the inset of figure 4). This fact evidences the energy transfer from Ce^{3+} to Tb^{3+} ions.

Moreover, the cerium emission overlaps the Tb^{3+} ${}^7F_6 \rightarrow {}^5H_5$, 5H_6 , ${}^7F_6 \rightarrow {}^5H_7$, 5D_1 , ${}^7F_6 \rightarrow {}^5L_{7,8}$, 5G_3 , ${}^7F_6 \rightarrow {}^5L_9$, 5D_2 , 5G_5 and ${}^7F_6 \rightarrow {}^5L_{10}$, 5G_6 , 5D_3 absorption (excitation) transitions, as can be appreciated from the spectra shown in figure 5.

Lifetime measurements performed on the Ce^{3+} emission in the co-doped ZPOCT glass were carried out by monitoring the emission at 340 nm after 290 nm laser pulsed excitation within the Ce^{3+} $4f \rightarrow 5d$ absorption transition. The Ce^{3+} emission decay is simple exponential, with a lifetime value of 20 ± 1 ns, which is shorter than the value of 26 ± 1 ns measured for the Ce^{3+} emission decay in the absence of Tb^{3+} ions [16]. The increase in the Ce^{3+} emission decay rate on co-doping with Tb^{3+} shows clear evidence of an energy transfer from Ce^{3+} to Tb^{3+} ions through a non-radiative mechanism. Lifetime measurements of the 5D_3 and 5D_4 levels of Tb^{3+}

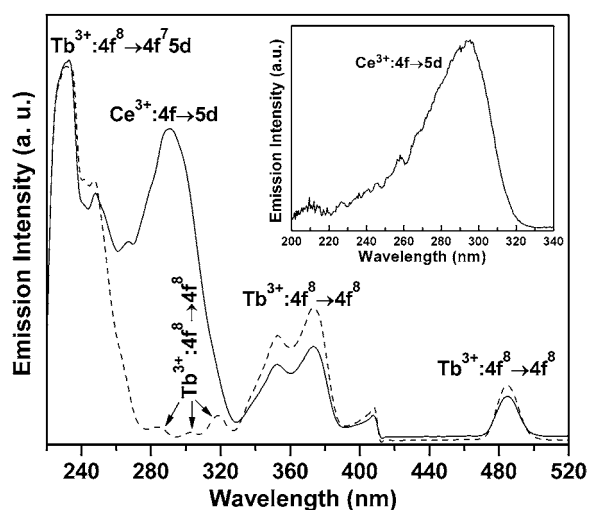


Figure 4. Excitation spectra monitored at 547 nm for ZPOT (dashed curve) and ZPOCT (solid curve). The inset displays the excitation spectrum monitored in the emission of Ce³⁺ at 350 nm for ZPOC [16].

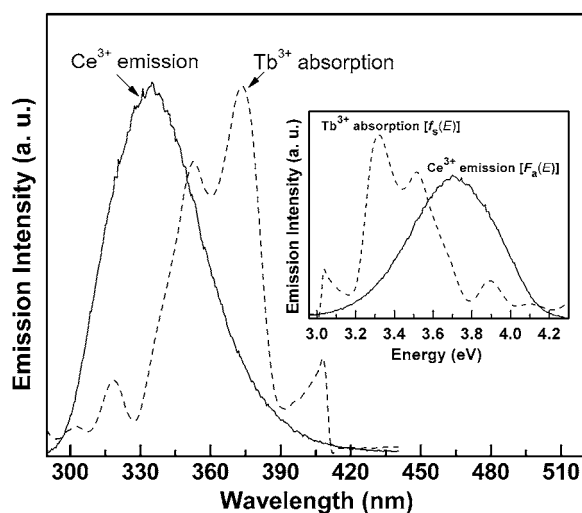


Figure 5. Overlap region between the Ce³⁺ emission (solid curve) and Tb³⁺ absorption (dashed curve). The inset shows the normalized line-shape functions. The Tb³⁺ absorption spectrum in the overlap region was taken from the ZPOT excitation spectrum displayed in the inset of figure 1.

were performed with Ce³⁺ excitation at 290 nm and with Tb³⁺ excitation at 352 nm. The Tb³⁺ emission decays were found to consist of a single-exponential decay with lifetime values of ~0.8–0.9 ms for the blue emissions and ~3.2 ms for the green emissions (see table 1).

The sensitizer–activator average interaction distance estimated from the concentrations of Ce³⁺ (8.0×10^{18} ions cm⁻³) and Tb³⁺ (8.0×10^{19} ions cm⁻³) in the host glass, assuming a random ion distribution, is so large (~28 Å) that the Ce³⁺ → Tb³⁺ energy transfer should not have occurred. Therefore, the energy transfer might take place in Ce³⁺–Tb³⁺ clusters formed in the host glass, in which it is expected that a short-range interaction mechanism might be

taking place. The very short lifetime measured for the Ce^{3+} emission [16] reflects that the $4f \rightarrow 5d$ absorption transitions are electric dipole allowed, whereas the long lifetime measured for the Tb^{3+} emissions reveals the forbidden nature of the $4f \rightarrow 4f$ transitions. Hence, it seems reasonable to think that the $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer could occur through an electric dipole–quadrupole (dq) interaction mechanism. In fact, the $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer in, for example, $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}^{3+}$ has been attributed to electric dq interaction [21]. However, in some other systems with low activator concentrations it has been demonstrated that the mechanism of sensitizing the Tb^{3+} luminescence through Ce^{3+} occurs by means of an electric dd interaction [22].

The critical interaction distance for energy transfer, either through an electrical dd or dq interaction mechanism, can be found from equations (2) and (4). The optical absorption spectrum of Tb^{3+} ions in the overlap region with the Ce^{3+} emission was hardly detectable due to the very weak intensity of the forbidden $4f\text{--}4f$ transitions. Thus, in equations (2) and (4) the Q_a integrated absorption coefficient of Tb^{3+} was estimated using the relationship derived by Blasse, $Q_a = 4.8 \times 10^{-20} \text{ eV m}^2 \cdot f_d$ [23]. The f_d electric dipole oscillator strength of the Tb^{3+} ion in glasses is usually considered to be of order 10^{-7} [24]. The overlap integral in equations (2) and (4) was calculated using the normalized line-shape functions of the cerium emission $f_s(E)$ and terbium absorption $F_a(E)$ in the overlap region, which are shown in the inset of figure 5. Using $Q_a = 4.8 \times 10^{-27} \text{ eV m}^2$ and the value estimated for the overlap integral ($5.5 \times 10^{-3} \text{ eV}^{-5}$) in equation (2), it is found that $R_{sa}^o(\text{dd}) = 3.5 \text{ \AA}$. On the other hand, the $R_{sa}^o(\text{dq})$ critical interaction distance for energy transfer through an electrical dq interaction mechanism was found from equation (4) using $f_q/f_d \sim 10^{-3}$ [21]. $R_{sa}^o(\text{dq})$ resulted in being 8.1 \AA . Both distances, $R_{sa}^o(\text{dd})$ and $R_{sa}^o(\text{dq})$, are rather smaller than the average separation distance assuming a random ion distribution ($\sim 28 \text{ \AA}$). This supports the fact that the $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer takes place in $\text{Ce}^{3+}\text{--}\text{Tb}^{3+}$ clusters formed in the host glass.

The P_{sa} experimental $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer probability can be obtained from equation (6) using the data obtained for the Ce^{3+} lifetime in the presence of Tb^{3+} ions and in the absence of energy transfer, which was taken from the experimental value obtained for the Ce^{3+} lifetime in the absence of Tb^{3+} ($\tau_s^o = 26 \text{ ns}$ [16]). The P_{sa} probability was found to be around $1.1 \times 10^7 \text{ s}^{-1}$. Then, the average interaction distance between the Ce^{3+} and Tb^{3+} ions involved in the energy transfer, assuming either an electric dd or dq interaction mechanism, can be estimated from equations (1) and (3) using the value obtained for P_{sa} . The $\bar{R}_{sa}(\text{dd})$ and $\bar{R}_{sa}(\text{dq})$ average interaction distances resulted in being about 4 and 9 \AA , respectively, which are similar to the corresponding critical interaction distances for energy transfer. Thus, the energy transfer in the $\text{Ce}^{3+}\text{--}\text{Tb}^{3+}$ clusters can be strongly enhanced because of the small interaction distances.

In order to evaluate whether the Ce^{3+} ion acts as a good sensitizer to the Tb^{3+} ion the η efficiency of energy transfer from Ce^{3+} to Tb^{3+} ions was obtained from decay time measurements using equation (8). The value found for η resulted in being about 23%. On the other hand, the efficiency of energy transfer was also determined using equation (9) and the Ce^{3+} emission spectra portrayed in figure 2 ((a) and (b) curves). The value found was about 20%. Thus, there is a reasonably good agreement between energy transfer efficiencies obtained from decay time data and that determined from emission spectra. This good agreement suggests that the $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer through a radiative mechanism can be neglected [25]. In fact, radiative energy transfer does not give rise to any reduction in the sensitizer decay time [26]. It can be noted that the energy transfer efficiency in the present co-doped glass is not very high. In principle it would be possible to increase it by increasing the Tb^{3+} concentration [27]. It has been found by Weber *et al* [14] that the solubility limit of a lanthanide ion (Nd^{3+}) in a calcium metaphosphate glass is about 11 mol% with respect to the alkaline-

earth metal ion. It is then reasonable to expect that the solubility limit of the Tb³⁺ ion in the present zinc phosphate glass is around 10 mol% with respect to the Zn²⁺ metal ion. However, on increasing the Tb³⁺ concentration it is not possible to estimate the average Ce³⁺-Tb³⁺ distance since these ions might be forming clusters of unknown number and size. For this reason, it is not possible to predict how much the energy transfer efficiency would increase at the maximum Tb³⁺ concentration.

In spite of the low efficiency of Ce³⁺ → Tb³⁺ energy transfer compared with the high efficiency of Ce³⁺ → Mn²⁺ energy transfer (53% [16]) for the same zinc metaphosphate glass host, an advantage of the first system is that the Tb³⁺ emission is faster than the slow Mn²⁺ emission, and therefore the response of the ZPOCT glass is more rapid than for the zinc metaphosphate glass activated with Ce³⁺ and Mn²⁺. Moreover, it is not possible to increase the Mn²⁺ concentration much as oxidation to Mn³⁺ ions could occur.

5. Summary and conclusions

The optical spectroscopy of Zn(PO₃)₂ glasses, singly doped with Tb³⁺ ions and doubly doped with Ce³⁺ and Tb³⁺ ions, has been investigated. By co-doping with Tb³⁺ ions the Ce³⁺ doped sample is observed to show the following features

- (i) an enhancement of the Tb³⁺ blue and green emissions after Ce³⁺ excitation with respect to those obtained with Tb³⁺ 4f⁸ → 4f⁸ direct excitation,
- (ii) an enhancement of the Tb³⁺ green emissions after Ce³⁺ excitation relative to those obtained with Tb³⁺ 4f⁸ → 4f⁷5d direct excitation,
- (iii) an increase in the decay rate of the Ce³⁺ emission, and
- (iv) a decrease of the Ce³⁺ overall emission.

These experimental observations reveal that a non-radiative energy transfer from Ce³⁺ to Tb³⁺ takes place in the co-doped glass.

A good agreement between the Ce³⁺ → Tb³⁺ energy transfer efficiency obtained from emission spectra and the one determined from decay time data is observed, which suggests that the Ce³⁺ → Tb³⁺ radiative energy transfer can be neglected.

The average interaction distance between Ce³⁺ and Tb³⁺ ions, estimated from the experimental energy transfer probability, resulted in being comparable with the critical interaction distance for energy transfer assuming an electrical dd or dq mechanism. These interaction distances are significantly lower than that estimated assuming a random ion distribution. This fact suggests that the dopant ions tend to cluster [28]. The ion clustering makes the Ce³⁺ and Tb³⁺ doubly doped zinc metaphosphate glass a suitable candidate for the design of efficient phosphors for ultraviolet (Ce³⁺ absorption) to blue–green frequency conversion.

Acknowledgments

We would like to thank the CBI chemical laboratory of the Universidad Autónoma Metropolitana-Iztapalapa for sharing its equipment. This work was supported by the CONACyT under project contract 43016-F. We also thank Erica Viviani (University of Verona) for expert technical assistance.

References

- [1] Boze E J, Hirata G A, Shea-Rohwer L E and McKittrick J 2003 *J. Lumin.* **104** 47
- [2] Jia D, Meltzer R S, Yen W M, Jia W and Wang X 2002 *Appl. Phys. Lett.* **80** 1535

- [3] Lahoz F, Daran E, Lifante G, Balaji T and Muñoz-Yague A 1999 *Appl. Phys. Lett.* **74** 1060
- [4] Strohhofner C, Kik P G and Polman A 2000 *J. Appl. Phys.* **88** 4486
- [5] Park S H, Lee D C, Heo J and Shin D W 2002 *J. Appl. Phys.* **91** 9072
- [6] Braud A, Girard S, Doualan J L, Thuau M, Moncorge R and Tkachuk A M 2000 *Phys. Rev. B* **61** 5280
- [7] Vega-Duran J T, Diaz Torres L A, Meneses-Nava M A, Maldonado-Rivera J L and Barbosa-García O 2001 *J. Phys. D: Appl. Phys.* **34** 3203
- [8] Caldiño G U, de la Cruz C, Muñoz H G and Rubio O J 1989 *Solid State Commun.* **69** 347
- [9] El Jouhari N, Parent C and Le Flem G 1996 *J. Solid State Chem.* **123** 398
- [10] Jia D, Zhu J, Wu B and E S 2001 *J. Lumin.* **93** 107
- [11] Caldiño G U 2003 *J. Phys.: Condens. Matter* **15** 3821
- [12] Caldiño G U 2003 *J. Phys.: Condens. Matter* **15** 7127
- [13] Martínez-Martínez R, García-Hipólito M, Ramos-Brito F, Hernández-Pozos J L, Caldiño U and Falcony C 2005 *J. Phys.: Condens. Matter* **17** 3647
- [14] Weber M J, Saroyan R A and Ropp R C 1981 *J. Non-Cryst. Solids* **44** 148
- [15] Tischendorf B, Otaigbe J U, Wiench J W, Pruski M and Sales B C 2001 *J. Non-Cryst. Solids* **282** 147
- [16] Caldiño U, Hernández-Pozos J L, Flores C, Speghini A and Bettinelli M 2005 *J. Phys.: Condens. Matter* **17** 7297
- [17] Förster Th 1959 *Discuss. Faraday Soc.* **27** 7
- [18] Dexter D L 1953 *J. Chem. Phys.* **21** 836
- [19] Paulose P I, Jose G, Thomas V, Unnikrishnan N V and Warriar M K R 2003 *J. Phys. Chem. Solids* **64** 841
- [20] de Graaf D, Stelwagen S J, Hintzen H T and de With G 2003 *J. Non-Cryst. Solids* **325** 29
- [21] Verstegen J M P J, Sommerdijk J L and Verriet J G 1973 *J. Lumin.* **6** 425
- [22] Marfunin A S 1979 *Spectroscopy, Luminescence and Radiation Centers in Minerals* (Berlin: Springer)
- [23] Blasse G 1969 *Philips Res. Rep.* **24** 131
- [24] Bettinelli M, Ingletto G, Polato P, Pozza G, Zanella G and Zannoni R 1996 *Phys. Chem. Glasses* **37** 4
- [25] Jaque D, Ramírez M O, Bausá L E, García Solé J, Cavalli E, Speghini A and Bettinelli M 2003 *Phys. Rev. B* **68** 035118
- [26] Henderson B and Imbusch G F 1989 *Optical Spectroscopy of Inorganic Solids* (Oxford: Clarendon/Oxford Science Publications)
- [27] Nag A and Kutty T R N 2005 *Mater. Chem. Phys.* **91** 524
- [28] Venikouas G E and Powell R C 1978 *Phys. Rev. B* **17** 3456