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Photoluminescence of Ce³⁺ and Mn²⁺ in zinc metaphosphate glasses

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Abstract

The spectroscopic characterization of zinc metaphosphate glasses, singly and doubly doped with Ce³⁺ and Mn²⁺ ions, is performed through excitation and emission spectra and decay time measurements. The weak yellow emission of Mn²⁺ is significantly enhanced by means of an efficient energy transfer from Ce³⁺ to Mn²⁺ ions. The efficiency of the energy transfer has been estimated based on spectroscopic data, and turned out to be about 53%. From spectroscopic data it can also be inferred that the energy transfer is nonradiative in nature and it takes place between Ce³⁺ and Mn²⁺ clusters formed in the glass through a short-range interaction mechanism. This impurity clustering appears to be a relevant finding for the design of efficient conversion phosphors of ultraviolet to visible light.

1. Introduction

The optical properties of trivalent rare-earth (RE³⁺) ions are very valuable when these ions are doped into materials due to the electronic transitions taking place within the partially filled 4f shell, or involving the 4f and 5d shells. As a consequence, these ions have contributed to the development of optical amplifiers and phosphors. Among these optical centres, the Ce³⁺ ion exhibits a broad band emission located at the border between the ultraviolet and visible ranges in crystals and glasses [1, 2]. Ce³⁺ activated materials have attracted renewed interest due to their favourable spectroscopic properties and the fact that Ce³⁺ can be incorporated into different host materials [3]. Moreover, in co-doped materials, the Ce³⁺ ion acts as a good sensitizer, transferring a part of its energy to activator ions such as Eu²⁺ [4] and Mn²⁺ [5, 6].

The Ce³⁺ ion in solids shows efficient broad band luminescence due to its 4f–5d parity allowed electric dipole transition. This ion has a high oscillator strength and a larger Stokes shift than the f–f ones typical of other RE³⁺ ions, owing to the extended radial wavefunctions of the 5d

state [7]. On the other hand, the Mn^{2+} transition metal ion also gives rise to a broad emission band in the visible range. In fact, the Mn^{2+} ion in solids produces green or red emission, depending on the host lattice, due to the forbidden d–d transition ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{G})$ [8–10] (in cubic symmetry). The Mn^{2+} ion emission appears to be characterized by a high quantum efficiency in phosphate glasses [7]. The optical absorption and EPR spectra of Mn^{2+} in zinc phosphate glasses have been interpreted on the basis of an octahedral coordination of the dopant [11].

Over several years phosphate glasses have attracted much attention because of their potential use in various optical devices. The phosphate glasses are relatively easy to prepare and show various interesting chemical and physical properties, which make them attractive as hosts for luminescent ions [12]. In particular, optical waveguides, glass–polymer composites and solid state laser sources have been manufactured with zinc metaphosphate glasses. Moreover, such glasses have been used as solders and welds between glassy and metallic parts in electronic circuits and television tubes because their thermal expansion coefficients are similar to that of many metals [13]. Considering the importance of finding efficient luminescent materials for the design of optical devices based on the zinc metaphosphate composition, in the present work the Mn^{2+} visible luminescence sensitized by Ce^{3+} ions in a Ce^{3+} - and Mn^{2+} -doped zinc metaphosphate glass has been analysed on the basis of photoluminescence measurements. To our knowledge no work has been reported on the luminescence of this host material doubly doped with cerium and manganese. In order to obtain a better understanding of the $\text{Ce}^{3+} \rightarrow \text{Mn}^{2+}$ energy transfer, emission, excitation and lifetime data for one-activator (Ce^{3+} or Mn^{2+}) glasses have also been obtained.

2. Experimental details

The molar compositions of the glasses studied were $\text{Zn}(\text{PO}_3)_2$ 99.9%– $\text{Ce}(\text{PO}_3)_3$ 0.1%, $\text{Zn}(\text{PO}_3)_2$ 99.0%– $\text{Mn}(\text{PO}_3)_2$ 1.0% and $\text{Zn}(\text{PO}_3)_2$ 97.9%– $\text{Ce}(\text{PO}_3)_3$ 0.1%– $\text{Mn}(\text{PO}_3)_2$ 2.0%. The three samples will be referred hereafter as ZPOC, ZPOM and ZPOCM, respectively. The zinc metaphosphate glasses were prepared by mixing appropriate quantities of ZnO (Aldrich 99+%), $\text{NH}_4\text{H}_2\text{PO}_4$ (Carlo Erba RPE), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich 99.99%) and MnO (Aldrich 99.99+%) in a sintered alumina crucible, and melting the composition for 2 h at 1250 °C. The melts were quenched onto a copper plate. In order to obtain thermal and structural stability the glasses were annealed for 12 h at 350 °C.

Luminescence spectra were recorded with a Perkin Elmer LS-50B spectrometer. Lifetime data of the Mn^{2+} emission and time-resolved spectra were obtained with this spectrometer operated in the phosphorescence mode. The decay curves of the Ce^{3+} emission were measured 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 measure the emission decay curves. The decay times were obtained from the emission decay curves using a deconvolution procedure, which takes into account the shape and the duration of the excitation pulse.

All measurements were carried out at room temperature and with the same instrumental parameters.

3. Results

The excitation and emission spectra displayed by the Ce^{3+} singly doped glass (ZPOC) are shown in figure 1. The emission spectrum was obtained with 280 nm excitation wavelength.

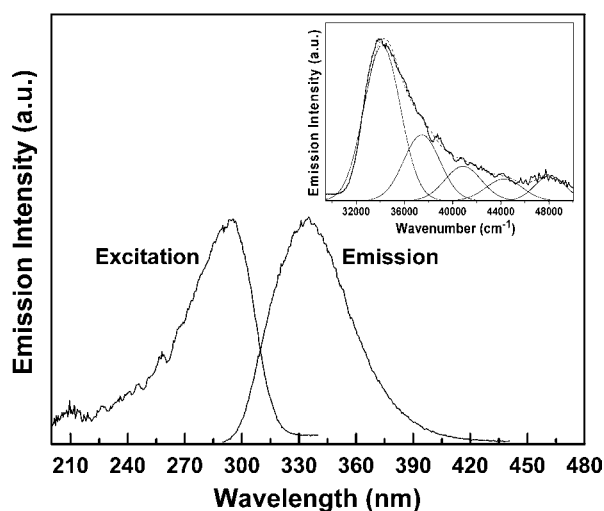


Figure 1. Excitation and emission spectra of ZPOC. The emission spectrum was obtained with 280 nm excitation and the excitation one was monitored at 350 nm. The inset shows the five 4f–5d bands of the Ce³⁺ (excitation) absorption.

It consists of a broad band in the near ultraviolet (UV) region peaking at 334 nm, giving maximum intensity for an excitation wavelength of 294 nm. The emission band is associated with the transition from the 5d¹ configuration to the 4f¹ one of the Ce³⁺ ions. The asymmetric spectral feature does not present the expected doublet associated with the transition from the excited state to the ²F_{5/2} and ²F_{7/2} levels of the 4f¹ ground state configuration, as reported in some crystals [4–6, 14] and glasses [15]. This lack of spectral structure has also been observed in Ce³⁺-doped Na–Gd phosphate glasses [16]. It is attributed to a strong inhomogeneous broadening, due to the disordered nature of the phosphate glass host. The excitation spectrum corresponding to this emission was monitored at 350 nm. It consists of a UV broad band peaking at 294 nm, which is associated with transitions from the 4f state to the 5d state of Ce³⁺ ions. This broad band is composed of five bands, as can be appreciated from the inset of figure 1, indicating full splitting of the ²D(5d) excited state. Then, the complete lifting of the degeneracy of the 5d orbitals suggests Ce³⁺ sites with symmetries lower than cubic. Rare-earth phosphate glasses have been studied using EXAFS [17], x-ray and neutron diffraction techniques [18, 19]. These results have revealed that samples containing the larger rare-earth ions, such as the Ce³⁺ ion, are coordinated to a number of oxygen atoms ranging between six and eight. Mössbauer spectroscopy [20], fluorescence line narrowing spectroscopy [21, 22] and molecular dynamics simulations [23] have shown that the rare-earth trivalent ion site symmetry in oxide glasses is very low, C_{2v} or C₁.

The Mn²⁺ singly doped glass (ZPOM) excited at 410 nm, which corresponds to the characteristic absorption of Mn²⁺-doped glasses, presents a yellow emission broad band centred at 560 nm. Figure 2 shows the excitation spectra of Mn²⁺ alone and Mn²⁺ in the presence of Ce³⁺ (ZPOCM glass). The excitation spectra were monitored at 570 nm, inside the yellow emission band of Mn²⁺. These spectra display several broad bands, which can be assigned, following Ravikumar *et al* [11], to ⁶A₁(S) → ⁴T₁(P), ⁴E(D), ⁴T₂(D), ⁴A₁, ⁴E(G), ⁴T₂(G) and ⁴T₁(G) excitation transitions of Mn²⁺ in octahedral symmetry. Thus, the large crystal field originating the Mn²⁺ yellow emission might be associated with an octahedral symmetry. An additional broad band at around 290 nm is observed in the ZPOCM co-doped sample, which is

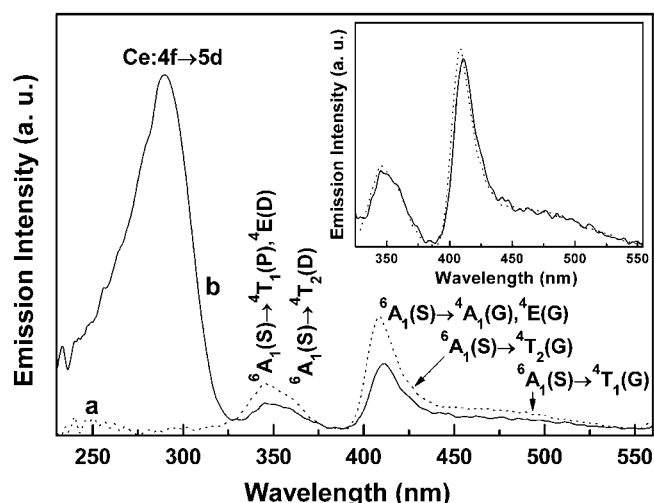


Figure 2. Excitation spectra monitored at 570 nm of (a) ZPOM and (b) ZPOCM. The inset shows the spectra normalized for the Mn^{2+} bands. The spectra were recorded with a delay time of 0.1 ms.

very similar to the UV excitation broad band observed in the ZPOC cerium singly doped glass, and hence, it must be associated with the $\text{Ce}^{3+} 4f \rightarrow 5d$ excitation transition. The presence of the $\text{Ce}^{3+} 4f \rightarrow 5d$ transition in the Mn^{2+} excitation spectrum indicates that the Mn^{2+} ions can be excited through the Ce^{3+} ions by means of an energy transfer process. The inset of figure 2 shows the excitation spectra monitored at 570 nm and normalized for the Mn^{2+} bands. From these spectra it can be noted that the excitation spectra of the singly doped glass (ZPOM) and the doubly doped one (ZPOCM) are virtually identical, which indicates that the variation of the Mn^{2+} energy levels is very small. Therefore, the perturbation of the ligand field around the Mn^{2+} ion induced by the Ce^{3+} ions is negligible. This behaviour is quite expected, as the exchange interaction between Mn^{2+} and Ce^{3+} ions is most probably very weak, in agreement with the results obtained for $\text{Mn}^{2+}\text{-Gd}^{3+}$ pairs in $\text{GdF}_3:\text{Mn}^{2+}$ by Vink *et al* [24].

The emission spectrum displayed by the ZOPCM doubly doped glass excited at 280 nm is shown in figure 3. It consists of the ultraviolet emission $5d \rightarrow 4f$ associated with Ce^{3+} ions and the yellow emission ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{S})$ characteristic of Mn^{2+} ions (inset of figure 3). The emission spectrum corresponding to the Ce^{3+} singly doped glass, measured in the same experimental conditions, is also shown for comparison. It is clear that the addition of Mn^{2+} ions in the Ce^{3+} -doped glass causes a decrease of the overall emission of Ce^{3+} ions. This fact and that Mn^{2+} cannot be excited at 280 nm provide evidence that energy transfer from Ce^{3+} to Mn^{2+} ions occurs by means of a nonradiative process.

Figure 4 displays the emission spectra of ZPOCM and ZPOM glasses, under excitation at 280 and 410 nm, in the Mn^{2+} emission region. The following can be noticed:

- (i) the absence of Mn^{2+} emission in ZPOM excited at 280 nm as a consequence that there is no excitation band for Mn^{2+} ions around this wavelength,
- (ii) a notable enhancement of the Mn^{2+} emission in ZPOCM excited at 280 nm with respect to that obtained with Mn^{2+} excitation at 410 nm, and
- (iii) the Mn^{2+} emission bandwidth and intensity in ZPOCM and ZPOM excited at 410 nm are practically the same, which might indicate the absence of back energy transfer from Mn^{2+} to Ce^{3+} , as it is reasonable to expect.

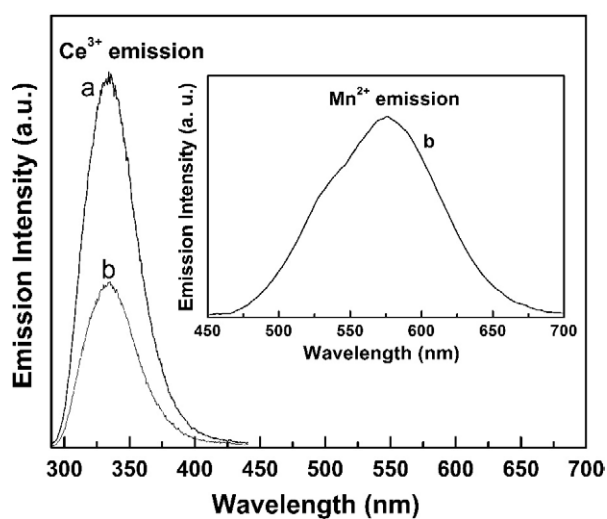


Figure 3. Emission spectra after 280 nm excitation of (a) ZPOC and (b) ZPOCM. The emission spectrum in the inset was recorded with a delay time of 0.1 ms.

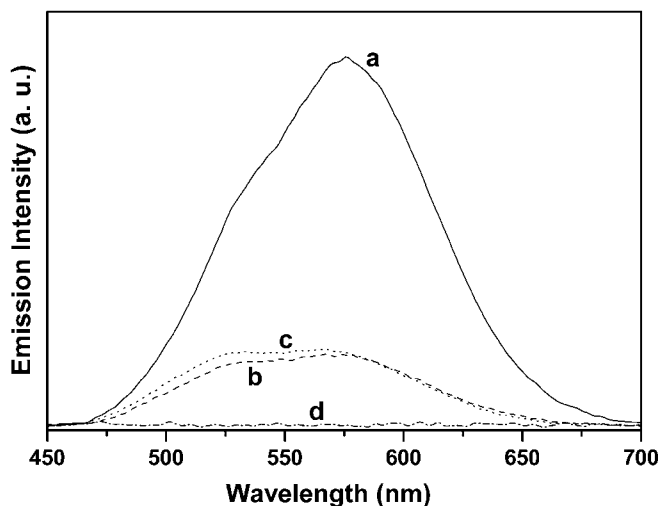


Figure 4. Emission spectra of ZPOCM excited at (a) 280 nm and (b) 410 nm, and ZPOM excited at (c) 410 nm and (d) 280 nm. The spectra were recorded with a delay time of 0.1 ms.

Lifetime measurements performed on the Ce³⁺ emission were carried out monitoring the emission at 340 nm after 290 nm laser pulsed excitation within the Ce³⁺ 4f → 5d absorption transition. In the absence of Mn²⁺ ion the Ce³⁺ emission decay is a simple exponential, with a lifetime value of 26 ns, which was found to be independent of the emission wavelength selected for the decay recording. This value represents the radiative lifetime of the emitting state [25] and is very similar to those found for Ce³⁺ in phosphate glasses [16, 26]. On the other hand, in the presence of Mn²⁺ the Ce³⁺ emission decay is even shorter, so it could not be properly resolved from the laser excitation pulse. The increase in the Ce³⁺ emission decay rate on co-doping with manganese can be attributed to the energy transfer from Ce³⁺ to Mn²⁺

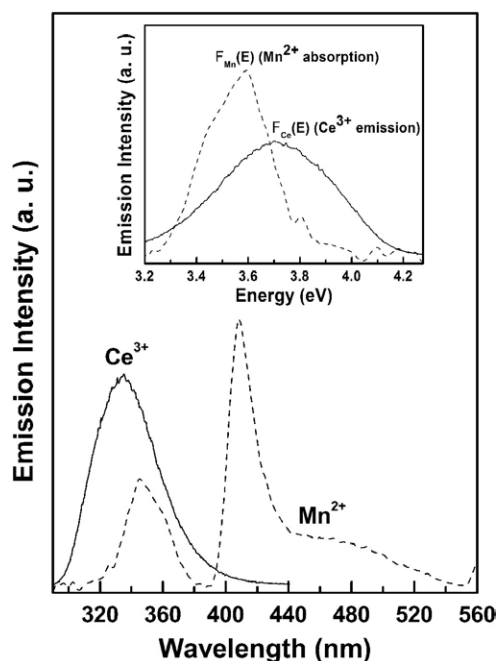


Figure 5. Overlap region between Mn^{2+} absorption (dashed curve) and Ce^{3+} emission (solid curve). The inset shows the normalized line-shape functions. The Mn^{2+} absorption spectrum was taken from the ZPOM excitation spectrum displayed in figure 2.

ions. Lifetime measurements on the Mn^{2+} emission at 570 nm were performed with Ce^{3+} excitation at 290 nm and with Mn^{2+} excitation at 410 nm. The Mn^{2+} emission decay was found to consist of a single-exponential decay with lifetime values of 14.7 and 14.2 ms when the Mn^{2+} is directly excited at 410 nm in ZPOCM and ZPOM, respectively, and 15.1 ms when the Mn^{2+} is excited via Ce^{3+} ions at 290 nm in ZPOCM.

4. Discussion

The enhancement of the Mn^{2+} emission in ZPOCM under Ce^{3+} excitation at 280 nm with respect to that obtained with Mn^{2+} direct excitation at 410 nm, the presence of the $\text{Ce}^{3+} 4f \rightarrow 5d$ absorption band in the excitation spectrum of the Mn^{2+} emission and the increase in the Ce^{3+} emission decay rate in the presence of Mn^{2+} provide clear evidence that energy transfer from Ce^{3+} to Mn^{2+} ions takes place in the doubly doped glass. Moreover, the transfer process is expected to occur considering that the cerium emission overlaps the $\text{Mn}^{2+} {}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_1(\text{P})$, ${}^4\text{E}(\text{D})$ and ${}^4\text{T}_2(\text{D})$ absorption (excitation) transitions, as can be appreciated from the spectra shown in figure 5.

The sensitizer–activator interaction distance estimated from the Ce^{3+} and Mn^{2+} ion concentration in the host glass, assuming a random ion distribution, is so large ($\sim 31 \text{ \AA}$) that the $\text{Ce}^{3+} \rightarrow \text{Mn}^{2+}$ energy transfer should not have occurred. Therefore, the energy transfer might take place in Ce^{3+} – Mn^{2+} clusters formed in the host glass, in which a short-range interaction mechanism can occur. A complete discussion of the microscopic mechanism of energy transfer has been published by Förster [27] and Dexter [28]. According to this theory the energy transfer through a multipolar interaction depends upon the overlap extent of the

emission spectrum of the sensitizer with the absorption spectrum of the activator, the relative orientation of the interacting dipoles and the spacing between these centres. The quite short lifetime measured for the Ce³⁺ emission reveals that the 4f → 5d absorption transition is electric dipole allowed, whereas the long lifetime measured for the Mn²⁺ emission reflects the forbidden nature of the 3d → 3d transitions. Therefore, it seems reasonable to assume that the Ce³⁺ → Mn²⁺ energy transfer could occur through an electric dipole–quadrupole (d–q) interaction mechanism. Under this assumption, the transfer rate W_{SA}^{dq} for an electric d–q interaction between sensitizer (Ce³⁺) and activator (Mn²⁺) ions is given by

$$W_{SA}^{dq} = \frac{3\hbar^4 c^4 f_q \lambda_S^2 Q_A}{4\pi n^4 \tau_S^0 f_d R_{SA}^8} \Omega, \quad (1)$$

where $\Omega = \int [F_S(E)F_A(E)/E^4] dE$ is the spectral overlap integral between the normalized line-shape functions of the sensitizer emission $F_S(E)$ and activator absorption $F_A(E)$, E being the transfer energy. The meaning of the remaining symbols in equation (1) has been described elsewhere [5, 6, 29]. The overlap integral Ω was calculated using the functions $F_{Ce}(E)$ and $F_{Mn}(E)$ in the overlap region, which are shown in the inset of figure 5. The function $F_{Mn}(E)$ was obtained from the excitation spectrum of the 570 nm Mn²⁺ emission displayed by the ZPOM glass (figure 2), since the optical absorption spectrum of Mn²⁺ ions was hardly detectable, even in high sensitivity conditions. The overlap integral resulted in being $0.8 \times 10^{-2} \text{ eV}^{-5}$. The oscillator strengths of the Mn²⁺ ion, f_q electric quadrupole and f_d electric dipole, are usually considered of order 10^{-10} and 10^{-7} , respectively [30–32]. The Q_A integrated absorption coefficient of Mn²⁺ was estimated using the relationship derived by Blasse, $Q_A = 4.8 \times 10^{-20} \text{ eV m}^2 \cdot f_d$ [33].

Let us now estimate the R_{SA}^0 (d–q) critical interaction distance for energy transfer, through an electrical d–q interaction mechanism, in order to corroborate that the energy transfer should not have occurred assuming a random ion distribution. The R_{SA}^0 (d–q) distance is defined as that for which the probability of transfer equals the probability of radiative emission of the sensitizer, that is, $W_{SA}^{dq} \tau_S^0 = 1$. Then, from equation (1),

$$R_{SA}^0 \text{ (d–q)} = \left(\frac{3\hbar^4 c^4 f_q \lambda_S^2 Q_A}{4\pi n^4 f_d} \Omega \right)^{1/8}. \quad (2)$$

Using the values estimated for Q_A and Ω in equation (2) it is found that R_{SA}^0 (d–q) = 8.57 Å. This distance is rather smaller than that obtained (~31 Å) assuming a random distribution of Ce³⁺ and Mn²⁺ ions. Therefore, it can be inferred that the Ce³⁺ → Mn²⁺ energy transfer seems to take place in Ce³⁺–Mn²⁺ clusters formed in the host glass.

The η energy transfer efficiency can give information on whether Ce³⁺ ion acts as a good sensitizer to Mn²⁺ ion. The η efficiency was measured using the following expression [34]:

$$\eta = 1 - \frac{I_S}{I_S^0}, \quad (3)$$

where I_S and I_S^0 are the intensities of the sensitizer in the presence and absence of the activator, respectively. Then, the efficiency of energy transfer from Ce³⁺ to Mn²⁺ ions, using equation (3) and the cerium emission spectra portrayed in figure 3, was found to be about 53%.

An alternative expression for the efficiency of energy transfer in terms of the transfer rate and τ_S^0 is given by [29]

$$\eta = \frac{W_{SA} \tau_S^0}{1 + W_{SA} \tau_S^0}. \quad (4)$$

So the experimental energy transfer rate can be obtained from equation (4):

$$W_{SA} = \frac{\eta}{(1 - \eta) \tau_S^0}. \quad (5)$$

Using the data obtained for η and τ_S^0 the $\text{Ce}^{3+} \rightarrow \text{Mn}^{2+}$ energy transfer rate was found to be around $4.3 \times 10^7 \text{ s}^{-1}$, which is slightly larger than the rate of radiative emission of the sensitizer ($3.8 \times 10^7 \text{ s}^{-1}$). Then, the \bar{R}_{SA} average interaction distance between the Ce^{3+} and Mn^{2+} ions involved in the energy transfer, assuming an electric d–q interaction mechanism, was estimated from equation (1), for which $W_{\text{SA}}^{\text{dq}} = 4.3 \times 10^7 \text{ s}^{-1}$, and the τ_S^0 sensitizer intrinsic lifetime in the absence of energy transfer was taken from the experimental value obtained for the Ce^{3+} lifetime in the absence of Mn^{2+} ($\tau_S^0 = 26 \text{ ns}$). The \bar{R}_{SA} interaction distance was found to be 8.44 \AA , which is a reasonable value, since it is similar to the R_{SA}^0 (d–q) critical interaction distance for energy transfer.

For comparison the transfer rate for an electric dipole–dipole (d–d) interaction mechanism, $W_{\text{SA}}^{\text{dd}}$, was estimated from its relation with the $W_{\text{SA}}^{\text{dq}}$ rate [5]:

$$W_{\text{SA}}^{\text{dd}} = \frac{R_{\text{SA}}^2 f_d}{\lambda_S^2 f_q} W_{\text{SA}}^{\text{dq}}. \quad (6)$$

The $W_{\text{SA}}^{\text{dd}}$ rate for an interaction distance of 8.44 \AA turned out to be $2.6 \times 10^5 \text{ s}^{-1}$, which is significantly smaller than the rate of Ce^{3+} radiative emission ($3.8 \times 10^7 \text{ s}^{-1}$). On the other hand, the R_{SA}^0 (d–d) critical interaction distance for energy transfer through an electrical d–d interaction mechanism estimated from equations (1) and (6) was found to be very small (3.67 \AA). Therefore, the $\text{Ce}^{3+} \rightarrow \text{Mn}^{2+}$ energy transfer through an electric d–q interaction mechanism appears to be significantly more probable than the electric dipole–dipole one. Moreover, the energy transfer efficiency, assuming an electric d–d interaction mechanism ($W_{\text{SA}} = W_{\text{SA}}^{\text{dd}}$ in equation (4)), turned out to be 0.6%. This value is not consistent with the measured energy transfer efficiency.

5. Summary and conclusions

The optical spectroscopy of zinc metaphosphate glasses, singly and doubly doped with Ce^{3+} and Mn^{2+} , has been investigated. The Ce^{3+} emission spectrum shows only one broad asymmetric band, and the emission does not present the characteristic doublet associated with the transition from the excited state to the $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ levels of the ground state configuration, as the splitting is masked by strong inhomogeneous broadening. The addition of Mn^{2+} ions in the Ce^{3+} -doped sample results in a notable enhancement of the Mn^{2+} yellow emission after Ce^{3+} excitation with respect to that obtained with Mn^{2+} direct excitation. This finding, along with the increase in the Ce^{3+} emission decay rate in the presence of Mn^{2+} , reveals that an energy transfer from Ce^{3+} to Mn^{2+} ions takes place in the doubly doped glass. The energy transfer occurs through a nonradiative process, since the presence of Mn^{2+} ions in the Ce^{3+} -doped sample results in a decrease of the sensitizer ion overall emission. The energy transfer efficiency measured from the Ce^{3+} emission intensities in the absence and presence of Mn^{2+} resulted in being about 53%. The spectroscopic data obtained suggest that the energy transfer occurs between Ce^{3+} and Mn^{2+} clusters formed in the glass through a short-range interaction mechanism. An electric dipole–quadrupole interaction seems to be the most probable mechanism occurring in the Ce^{3+} – Mn^{2+} complexes. The critical interaction distance is significantly lower than the average distance between Ce^{3+} and Mn^{2+} , calculated assuming a random dopant distribution. This behaviour indicates that the dopant ions tend to cluster [35]. The impurity clustering makes the Ce^{3+} and Mn^{2+} doubly doped zinc metaphosphate glass an interesting material for the design of efficient phosphors for UV (Ce^{3+} ion absorption) to yellow (Mn^{2+} ion emission) frequency conversion.

Acknowledgments

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