Optical properties of manganese in barium phosphate glasses

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Abstract

Spectroscopic studies of optical properties of manganese ions in barium phosphate glasses prepared by adding 1–20 mol% of Mn_2O_3 in the glass composition were performed. Depending on the processing conditions, both Mn^{2+} and Mn^{3+} species were present, as indicated by the absorption spectra. However, emission and excitation spectra measurements showed the existence of only one luminescent center, even at cryogenic temperatures, ascribed to Mn^{2+}. Although the measured luminescence decay time curves were non-exponential, a comparison of different samples indicated that two distinct luminescence effects are involved. Exchange interaction between Mn^{2+} ions is responsible for the emission red shift associated with the manganese concentration increase. Moreover, the luminescence decay time indicates that a non-radiative energy transfer is also involved in the deexcitation process.
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1. Introduction

Many 3d-transition metals can exist in more than one oxidation state in glasses [1,2]. For several reasons, it seems interesting to explore these systems from the point of view of their optical properties. In recent years, a promising application has been demonstrated for the fabrication of a three-dimensional colored image inside a transparent material [3]. This experiment involved an oxidation of Mn^{2+} to Mn^{3+} in Mn–Fe ions co-doped silicate glasses. On the other hand, surprisingly large quantum efficiencies of Mn^{2+} luminescence at room temperature were reported in phosphate glasses [4]. Besides that, Mn^{3+} luminescence has been observed in both silicate and borate glasses [5]. Concentration dependence studies of Mn^{2+} luminescence in phosphors indicated a lifetime shortening of impurity emission with increasing Mn^{2+} [6,7]. This decrease is important for

some potential applications in plasma display panels and it was explained as due to magnetic interactions between pairs of Mn^{2+} ions.

Phosphate glasses are particularly attractive hosts because they can incorporate larger concentrations of transition metal ions than many other compositions, keeping the useful properties of the material. Furthermore, they are relatively easy to prepare. The aim of the present work was to explore these characteristics from the point of view of optical characterization of Mn^{2+} and Mn^{3+} in manganese-doped barium phosphate glasses prepared with different concentrations of dopant ion.

2. Experimental procedures

Phosphate glasses with composition $40BaO \cdot 60P_2O_5$ (mol%) were produced by mixing different inorganic precursors. P_2O_5 or $NH_4H_2PO_4$, and $BaCO_3$ were mixed during 30 min at room temperature and heated to 450 °C in an alumina crucible in air. The material was main-

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tained at this temperature for 1 h to decompose the phosphorus pentoxide leading to the release of ammonia and water. The material was then heated to temperatures in the range of 1100–1300 °C, and kept at these temperatures for 0.5–2 h, for the liquid homogenization. The mixing and heating steps were similar for all glasses, but the melting temperature and time for homogenization were different, as shown in Table 1. The liquid was stirred, and cast in a heated aluminum mold. Glasses were then annealed at 490 °C for 2 h, and finally cooled to room temperature by shutting off the power to the furnace, that is cooling due to the furnace thermal inertia. Glasses were doped with 1–20 mol% of Mn_2O_3.

The valence state of the manganese ions in the glass (see Table 1) depends on the type of inorganic precursor used to produce the glass: P_2O_5 or $NH_4H_2PO_4$. If P_2O_5 is used as precursor, the atmosphere is oxidative. If $NH_4H_2PO_4$ is used as precursor, the atmosphere will be reductive. The decomposition of $NH_4H_2PO_4$ evolves nitrogen and hydrogen which are responsible for the reductive atmosphere. Consequently, glasses with different colors are produced: pale yellow when Mn^{2+} is present and purple when Mn^{3+} is present.

In this work absorption, emission, excitation spectra and luminescence decay time were measured. The absorption spectra were taken using a double-beam spectrophotometer (Cary/Olis, model 17D). In the emission and excitation spectra apparatus, the sample was excited by a 300 W xenon lamp, focused into a 0.25 m long Ebert monochromator and modulated by a mechanical chopper. Luminescence was collected at right angles to the excitation direction, dispersed through a 0.5 m grating monochromator and detected with an InGaAs photomultiplier and a lock-in amplifier. For low temperature measurements, a helium closed-circuit refrigerator cryostat was employed. The lifetimes were measured using a pulsed laser excitation (4 ns) from a tunable optical parametric oscillator pumped by the second harmonic of a Q-switched Nd-YAG laser. The signal was detected by a S1 photomultiplier and ana-

lyzed by a digital 200 MHz oscilloscope. All the luminescence decay times were measured at room temperature.

3. Results and discussion

The absorption spectra of phosphate glasses containing 2.5, 5, 10 and 20 mol% of Mn_2O_3 are shown in Fig. 1. All spectra contain a narrow band at 410 nm. This band can be assigned to the $^6A_1(S) \rightarrow {}^4A_1(G)$, ^4E transition of Mn^{2+}, which has a $3d^5$-electron configuration [1,2]. In this case, all transitions are spin forbidden and therefore the intensity is much less than for spin allowed transitions. A broad band can also be observed at 515 nm which corresponds to the $^5E_g \rightarrow {}^5T_{2g}$ transition of Mn^{3+}, which has a $3d^4$-electron configuration [1,2]. In octahedral symmetry, Mn^{3+} has a single spin allowed transition. Depending on the preparation conditions it was possible to increase the fraction of Mn in a particular charge state. This is shown in Fig. 2 for three different samples prepared with 10 mol% of Mn_2O_3. We remark that when the amount of Mn^{2+} is largest, the transparence of a sample is preserved near 300 nm. On the other hand, the larger the fraction of Mn^{3+}, the larger the red shift of the absorption saturation wavelength. This absorption saturation was observed for wavelengths shorter than 400 nm, indicating the occurrence of a strong absorption between 200 and 300 nm. This band should be an oxygen → metal charge transfer [8], Mn^{3+} in this work. If Mn^{2+} was predominant, samples would be transparent. On the other hand, samples with a larger fraction of Mn^{3+} became purple. For low temperature absorption measurements, significant changes in absorption were not detected. The 515 nm band was blue shifted to 508 nm and its width decreased.

Glass samples were optically excited in the region of the main absorption peaks. Even at low temperature, only one emission band was detected, with a red shift associated with an increase of the manganese concentration (Fig. 3(a)). This is typical of Mn^{2+} ions in phos-

Table 1
Processing parameters of glasses produced in the present work

Glass sample	Precursor type	Mn_2O_3 concentration (mol%)	T (°C)[a]	t (min)[b]	Probable Mn valence state
S1	$NH_4H_2PO_4$	1	1300	30	Mn^{2+}
S2	P_2O_5	2	1300	30	Mn^{2+}, Mn^{3+}
S3	$NH_4H_2PO_4$	2.5	1300	80	Mn^{2+}, Mn^{3+}
S4	$NH_4H_2PO_4$	5	1300	80	Mn^{2+}, Mn^{3+}
S5	$NH_4H_2PO_4$	10	1300	80	Mn^{2+}, Mn^{3+}
S6	$NH_4H_2PO_4$	20	1300	80	Mn^{2+}, Mn^{3+}
S7	P_2O_5	10	1100	30	Mn^{2+}, Mn^{3+}
S8	$NH_4H_2PO_4$	10	1300	20	Mn^{2+}, Mn^{3+}
S9	$NH_4H_2PO_4$	10	1300	30	Mn^{2+}

[a] T = melting temperature.
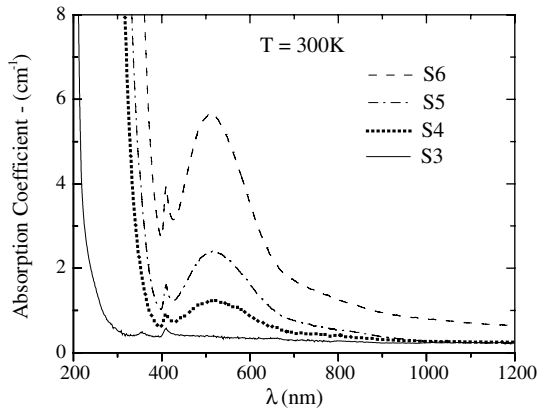[b] t = homogenization time.

Fig. 1. Optical absorption spectra, at room temperature, of barium phosphate glasses prepared with 2.5, 5, 10 and 20 mol% of Mn_2O_3 under reducing conditions.
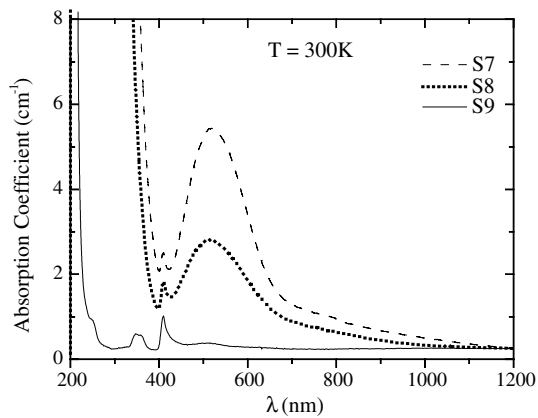

Fig. 2. Optical absorption spectra, at room temperature, of 10 mol% Mn_2O_3 phosphate glass samples prepared under reducing and oxidizing conditions.
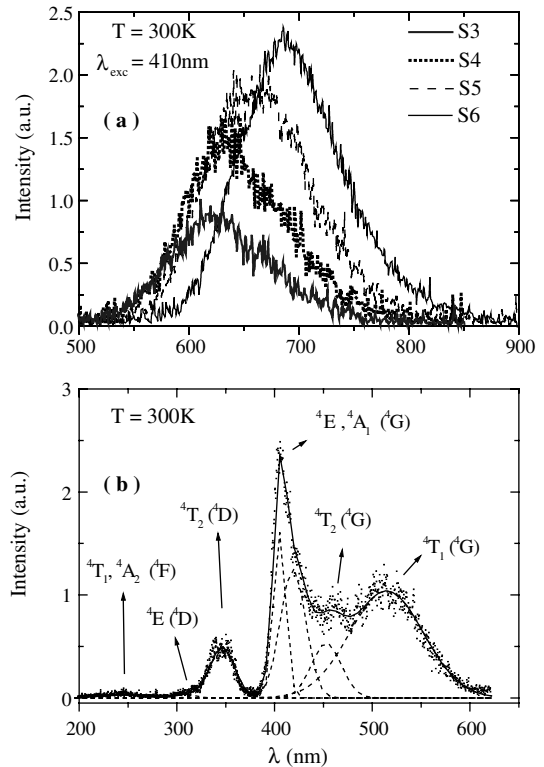

Fig. 3. Emission spectra obtained by excitation at 410 nm (a) of phosphate glass samples prepared with different concentrations of Mn_2O_3 under reducing conditions. (b) Excitation spectrum with the monitoring wavelength set at maximum of the emission band. All measurements were made at room temperature.

phors and was previously explained by magnetic interactions between pairs of Mn^{2+} ions [6,7,9]. The emission band for glass samples containing 1 mol% of Mn_2O_3 was observed around 617 nm and for a 10 mol% of Mn_2O_3 around 663 nm. A large spectral bandwidth of nearly 2500 cm^{-1} is noted. Moreover, a larger red shift of the emission peak is seen $(\Delta(1/\lambda) = 1125 \, cm^{-1})$ when compared to the 343 cm^{-1} energy shift observed for $MgAl_2O_4$:Mn^{2+} crystals [6]. The corresponding excitation spectra were similar, therefore only one experimental curve is shown in Fig. 3(b). This spectrum shows a complex profile involving several weak excitation bands which can be unambiguously identified as coming from Mn^{2+} transitions, when compared to Tanabe–Sugano diagrams for a d^5-electron configuration [1,2]. Bands at nearly 515, 405 and 346 nm can be identified and related to $^6A_1(S) \rightarrow {}^4T_1(G)$, $^6A_1(S) \rightarrow {}^4A_1(G)$, $^4E(G)$ and $^6A_1(S) \rightarrow {}^4T_2(D)$ transitions, respectively. Evaluation of crystal field parameters from the bands in the electronic spectra yields a crystal field parameter

$Dq = 839 \, cm^{-1}$, Racah parameter $B = 772 \, cm^{-1}$ and consequently $Dq/B = 1.09$.

Decay time measurements were performed at 300 K to obtain a deeper insight into the luminescence of Mn ions in phosphate glasses. The laser excitation was set at 480 nm and the temporal analysis of the luminescence was performed at wavelengths around the maximum intensity of the emission band. Most of the decay curves could not be fitted by a single exponential process. Site-to-site differences in radiative and non-radiative transition probabilities may be one of the possible sources for this distribution, mainly for samples with smaller Mn concentration. This is caused by disorder inherent in glassy solids. For glass samples with smaller concentration of Mn, a good fitting was obtained assuming two exponential functions for the decay processes. For concentrations <5 mol% of Mn, there was no change in the estimated decay times; a fast component varying between 1.5 and 3.8 ms indicated the existence of Mn pairs (16–28%) and a longer component of 17.5–21 ms was associated with the emission of isolated ions (84–72%), as inferred from the ratio between the intensities of each decay time component ($t = 0$ s). Above 5 mol% of Mn, the longer component decreased by a factor of two. This decrease is an indication of luminescence concentration quenching.

Another possible mechanism would be the occurrence of non-radiative energy transfer. To verify such transfer, a fit of the experimental data to a non-exponential decay model was tried. The Mn-luminescence decay was analyzed using the Inokuti–Hirayama [10] solution for the donor luminescence decay assuming that no excitation migration is present.

$$\overline{\rho}_D(t) = C \exp\left[(-t/\tau_D) - \gamma\sqrt{t}\right], \tag{1}$$

where τ_D is the lifetime of isolated donor and γ ($s^{-1/2}$) is the transfer constant that is dependent on the donor and acceptor concentrations and C is a constant. The total lifetime of donor was calculated using the expression:

$$\frac{1}{\tau} = \frac{1}{\tau_D} + \gamma^2. \tag{2}$$

The results concerning the adjustment of experimental luminescence decay data to this model are shown in Table 2.

Data were analyzed considering two different approaches: decay time dependence on impurity concentration of samples containing almost entirely Mn^{2+} species and samples exhibiting both Mn^{2+} and Mn^{3+} species.

Fig. 4 shows the luminescence decay for samples S1 (1 mol% of Mn) and S9 (10 mol% of Mn). Both samples contain essentially Mn^{2+} species. The full lines correspond to a fitting of experimental curves according to the non-exponential decay model of Inokuti–Hirayama. Fig. 5 shows the results concerning samples with 2 (sample S2) and 10 mol% (sample S8) of Mn which contains both Mn^{2+} and Mn^{3+} species. Curves of samples with the smallest Mn content were well fitted to the Inokuti–Hirayama model as indicated on both figures. The sample with the smallest Mn content has the smallest γ (see the transfer parameters in Table 2). The long lifetimes observed are a characteristic of isolated Mn^{2+} ions and were similar to results obtained by the decay time adjustment for two exponential decays. In general, γ increases with the Mn concentration, as expected. On the other hand, the decay in glass samples with Mn concentrations greater than 5 mol% was not fitted by the Inok-
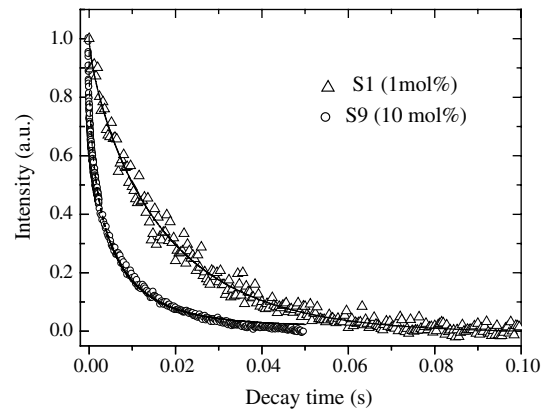

Fig. 4. Luminescence decay curves of Mn^{2+}-doped phosphate glasses (1 and 10 mol%) taken at room temperature. Laser excitation was made at 480 nm and the emission was monitored at 620 and 640 nm respectively. The curves are the best fit of Eq. (1) to the data.
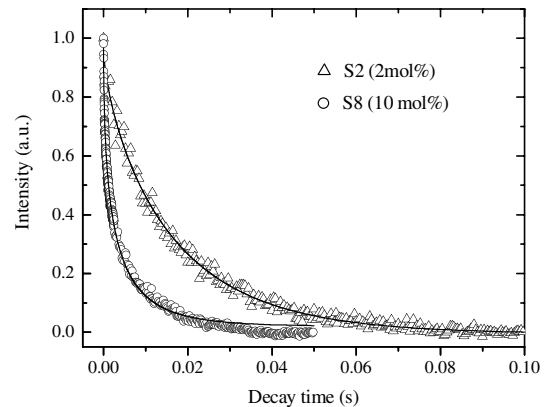

Fig. 5. Decay curves at room temperature of Mn^{2+}/Mn^{3+}-doped phosphate glasses (2 and 10 mol%) prepared under oxidizing conditions. Laser excitation was made at 480 nm and the emission was monitored at 620 and 640 nm respectively.

uti–Hirayama theory. Both Figs. 4 and 5 showed that although the model can account for the beginning of the decay, there is probably another effect contributing for all the decay process. However, we note that the transfer parameter, γ, increases linearly with the Mn

Table 2
Luminescence decay analysis considering the Inokuti–Hirayama model for Mn-doped barium phosphate glasses prepared under different conditions

Sample	Mn_2O_3 (mol%)	Mn valence state	λ_{em} (nm)	Parameters[a]		
				γ	τ_D (ms)	τ (ms)
S1	1	Mn^{2+}	620	2.6	24	21
S2	2	Mn^{2+}, Mn^{3+}	620	3.3	25	20
S3	2.5	Mn^{2+}, Mn^{3+}	614	5.6	33	16
S4	5	Mn^{2+}, Mn^{3+}	640	4.5	27	17
S6	20	Mn^{2+}, Mn^{3+}	680	38.1	24	0.67
S7	10	Mn^{2+}, Mn^{3+}	640	18.3	40	2.8
S8	10	Mn^{2+}, Mn^{3+}	640	18.6	29	2.6
S9	10	Mn^{2+}	640	14.5	28	4.8

[a] γ = transfer constant; τ_D = lifetime of the donor; τ = total lifetime deduced from Eq. (2).

concentration as expected from the applied fitting model.

From Table 2 we observed a remarkable shortening of the lifetime from nearly 20 ms to 3 ms for samples with 1 and 10 mol% of Mn, respectively. We remark that when comparing samples S1 and S2 with smaller impurity concentrations, a change in the decay time values is not observed. This might be an indication that there is no energy transfer between Mn^{2+} and Mn^{3+} species in this range. A similar effect is observed when samples with 10 mol% containing different ratios of Mn^{2+}/Mn^{3+} ions (samples S7, S8 and S9) were compared. The reduction of decay time with the increase of impurity concentration should thus be due to interactions between Mn^{2+} ions. These effects are stronger for 20 mol% Mn-doped samples for which a reduction of decay time by a factor of nearly five is observed.

4. Conclusions

The experimental results concerning absorption spectra of manganese-doped barium phosphate glasses, prepared under different processing conditions and different Mn concentrations, indicate the possibility of obtaining samples which contain essentially Mn^{2+} or both Mn^{2+} and Mn^{3+} species. However, emission and excitation spectra measurements indicated the existence of only one luminescent center, even at cryogenic temperatures, ascribed to Mn^{2+} ions. The red shift emission associated with increasing Mn concentration showed that exchange interaction between pairs of Mn^{2+} was involved, as observed in crystalline systems. Although exchange interaction effect also induces a shortening of decay time, the temporal analysis of luminescence decay showed that the non-exponential dependence was well described by the Inokuti–Hirayama model involving a non-radiative energy transfer between Mn^{2+} ions. Therefore both effects should be considered to better describe the Mn^{2+} luminescence in these glass systems.

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