Optical absorption and electron paramagnetic resonance study of Cr^{3+}-doped phosphate glasses

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Abstract. We report in this paper optical absorption and electron paramagnetic resonance (EPR) results obtained on Cr^{3+}-doped phosphate glasses. Optical absorption allowed us to evaluate the crystal-field parameters D_q, B and C. Electron paramagnetic resonance measurements indicate that Cr^{3+} ions are located in sites with low symmetry and a relatively large zero-field splitting. Both electron paramagnetic resonance and optical absorption data show that the chemical bonds of Cr^{3+} ions with the ligands are rather covalent in nature but that the ionic contribution to those bonds decreases in the order: PBa > PBaK > PBaKMg. Furthermore, it is found from this study that the crystal-field strength increases in the order: PBa < PBaK < PBaKMg.

1. Introduction

Over the last few decades, great importance has been attached to glasses doped with rare-earth or transition-metal ions because of the interesting spectroscopic properties of their $4f^N$ and $3d^N$ electrons, respectively. Among transition-metal ions, Cr^{3+} continues to attract much more attention because of its favourable absorption and emission properties when incorporated in octahedral sites of a host material. The relative positions of the excited $^4T_{2g}$ and ^2E states of this ion depend on the crystal field strength. In a weak field ($D_q/B < 2.3$), $^4T_{2g}$ is the lowest excited state and emission arises from the $^4T_{2g} \rightarrow ^4A_{2g}$ spin-allowed transition. These $^4T_{2g} \rightarrow ^4A_{2g}$ broad emission bands are of interest for applications in lasers [1, 2] and solar concentrators [3, 4]. This transition is also responsible for efficient sensitization of Nd^{3+} ions if energy transfer from Cr^{3+} to Nd^{3+} is more probable than radiative or nonradiative relaxation of the $^4T_{2g}$ state [5]. Furthermore, Cr^{3+} is useful for obtaining information about the amorphous local environment.

Among oxide glasses, phosphate glasses are very important from the point of view of technological effectiveness and preservation of the useful properties of the material upon introduction of a significant amount of active ions [6]. They are also relatively easy to prepare and offer an important range of compositional possibilities with which it is possible to tailor physical and chemical properties of interest for specific technological applications.

Optical absorption and electron paramagnetic resonance (EPR) are recognized as powerful tools for probing the local environment of a paramagnetic impurity and mapping the crystal field [7, 8]. In a previous paper [9], we presented the results of an optical and EPR study of phosphate glasses separately doped with Cr^{3+}, Cu^{2+} and Mn^{2+}. In this paper we have focused our study on Cr^{3+}-doped phosphate glasses. We have also examined the effect of the starting glass composition on the spectroscopic properties of the Cr^{3+} ion.

2. Experimental details

Chromium-doped phosphate glasses were prepared by melting the starting reagents in a platinum crucible, in an electric furnace heated to 1350 °C in an air atmosphere. The melt was then poured onto a stainless plate and annealed at 400 °C. Finally, the samples were polished for optical measurements or ground for the EPR study. The glasses were prepared in the following two compositions:

- PBaK: 60 mol% of $(NH_4)_2HPO_4$, 20 mol% of KH_2PO_4, 20 mol% of $BaCO_3$
- PBaKMg: 26 mol% of $(NH_4)_2HPO_4$, 27 mol% of KH_2PO_4, 39 mol% of $BaCO_3$, 8 mol% of MgO.

These compositions were selected because they allow us to dissolve a significant amount of chromium oxide without precipitation. Glasses were doped by adding x wt% of chromium oxide Cr_2O_3 to the starting composition (x varies in the range 0.005–1).

Optical absorption was measured on the diluted sample only at room temperature. EPR spectra were recorded at 9.22 GHz, with a constant power (0.2 mW) and the same weight for all the samples in the temperature range from 100 K to 400 K. Polycrystalline DPPH (diphenylpicrylhydrazyl) with an effective g factor of 2.0036 ± 0.0002 was used as the standard g marker. The energy accuracy for sharp bands is ± 5 cm^{-1}.
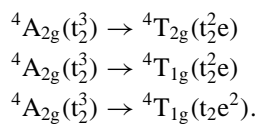
3. Results and discussion

3.1. Optical absorption study

The optical absorption spectrum of the diluted Cr^{3+}-doped PBaKMg glass exhibits three principal bands situated at 658, 455 and 294 nm (figure 1(b)), while that of the PBaK glass shows only two bands at 657 and 450 nm with the band at higher energy obscured (figure 1(a)). The low-energy band in the two optical spectra shows fine structure.

The observed bands in the optical spectra can be easily interpreted in terms of crystal-field theory. The Cr^{3+} ions are usually assumed to occupy approximately octahedral symmetry sites in inorganic solids. This is due to the ionic radius and the strong ligand-field stabilization energy of Cr^{3+} ions in sixfold coordination [10, 11]. The parity-forbidden d–d transitions can be partially allowed by the weak distortion of the crystal field or by instantaneous distortion due to molecular vibrations [11, 12].

The assignment of the bands is given in table 1. The spin-allowed transitions ($\Delta S = 0$) are broad because they are associated with a change in the electronic configuration as seen below:

$$^4A_{2g}(t_2^3) \rightarrow {}^4T_{2g}(t_2^2e)$$
$$^4A_{2g}(t_2^3) \rightarrow {}^4T_{1g}(t_2^2e)$$
$$^4A_{2g}(t_2^3) \rightarrow {}^4T_{1g}(t_2e^2).$$

Further, each of the two absorption spectra shows fine structure in the vicinity of the $^4A_{2g} \rightarrow {}^4T_{2g}$ band (figure 1). Following the Fano-antiresonance interpretation [13], this structure has been attributed to the two spin-forbidden transitions $^4A_{2g} \rightarrow {}^2E$ and $^4A_{2g} \rightarrow {}^2T_{1g}$. These transitions acquire their spin-allowed character via spin–orbit interaction with the broad $^4A_{2g} \rightarrow {}^4T_{2g}$ transition. They are dips because of the destructive interference with the $^4T_{2g}$ vibronic quasi-continuum which causes cancellation of observed intensities as well as a change in the original peak position and shape [14]. They are sharp because there is no change in the electronic configuration (t_2^3) [5, 14].
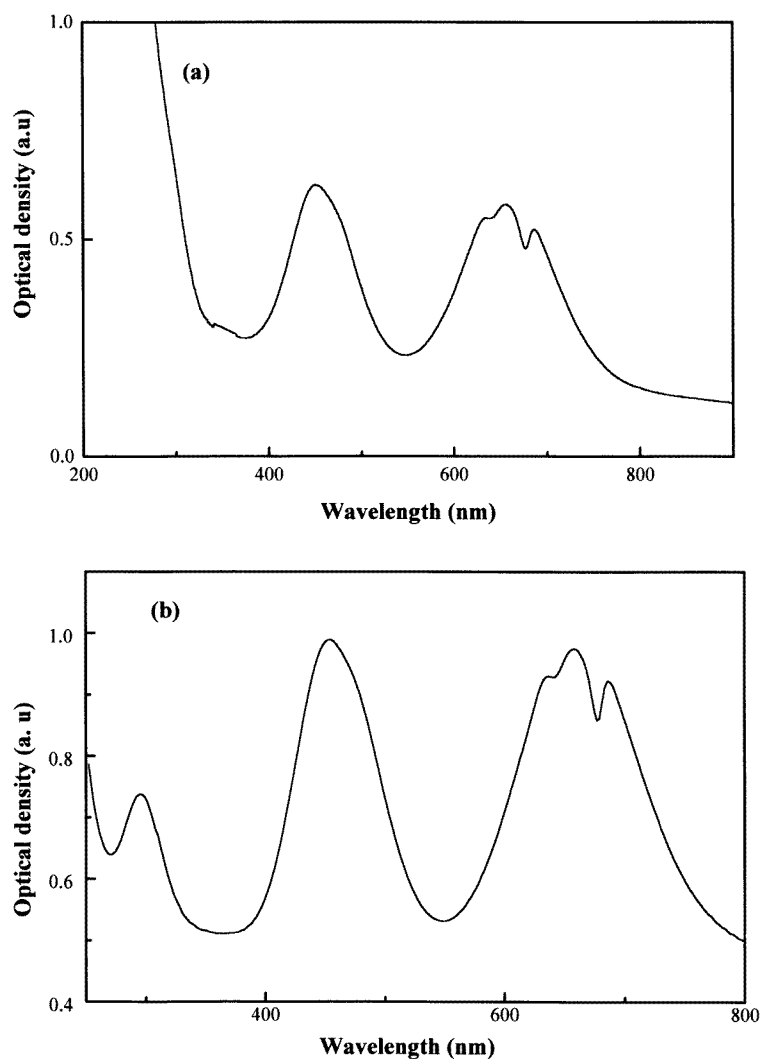
Figure 1. Optical absorption spectra of the diluted samples ($x = 0.1$ wt%) obtained at room temperature: (a) for the PBaK and (b) for the PBaKMg glass systems.

The disappearance of the $^4A_{2g} \rightarrow {}^4T_{2g}(P)$ transition band in the spectrum of the PBaK glass can be explained by a decrease in the transparency. This is due to an increase in the ultraviolet cut-off wavelength with an increment in the atomic number and a decrease in the cationic field strength [15, 16] when replacing Mg with Ba. From this result, it seems that the PKBaMg glass system is more interesting than PBa and PBaK glasses for efficient optical pumping because it permits the excitation of a significant number of doping ions [17].

On the basis of the preceding band assignment and by the use of the energy expression given by Adam *et al* for Cr³⁺ ions in octahedral symmetry [18], the crystal-field parameters D_q, B and C for the investigated glasses were estimated (table 2). As can be seen, the PKBaMg glasses exhibit a relatively large value of D_q/B. This means that the crystal-field

Table 1. Band assignment of the optical spectra supposing Cr^{3+} ions to be located at nearly octahedral sites and following the Fano-antiresonance interpretation.

Electronic transition	Band position	
	PBaK glass	PBaKMg glass
$^4A_{2g} \rightarrow {}^2E_1$	14 800	14 770
$^4A_{2g} \rightarrow {}^4T_{2g}$	15 220	15 200
$^4A_{2g} \rightarrow {}^2T_{1g}$	15 650	15 630
$^4A_{2g} \rightarrow {}^4T_{1g}(P)$	22 220	21 980
$^4A_{2g} \rightarrow {}^4T_{1g}(G)$	—	34 010

Table 2. Spectroscopic properties of Cr^{3+} in different phosphate glass systems.

Phosphate glass system	$E(^4T_{2g}) \rightarrow E(^4A_{2g})$ (cm^{-1})	D_q (cm^{-1})	B (cm^{-1})	C (cm^{-1})	D_q/B
PBa [15]	15 100	1510	750	—	2.01
PBaK [This work]	15 220	1522	708	3356	2.15
PBaKMg [This work]	15 200	1520	697	3373	2.18

strength increases in the order PBa < PBaK < PBaKMg. The shift in the absorption bands to higher energies also confirms this result. We think that this increase is a result of an important distortion of the polyhedron formed glass structural network [15], which is due to the different sizes of the species forming the glass. It has been shown experimentally [19] and theoretically [20] that $10D_q$ strongly depends upon the metal–ligand distance. The D_q values obtained in this work suggest that the average distance between the Cr^{3+} and the ligand is the same in the PBaK and PBaKMg glass systems. The Racah parameter B can be regarded as a measure of inter-electronic repulsion in the d shell; the larger the B value, the more the electrons are localized on the transition-metal ion. By comparing the B values (table 2), we can say that the ionic contribution to the chemical bonds between Cr^{3+} ions and the ligands decreases in the order PBa > PBaK > PBaKMg and the bonds are more covalent in PBaKMg than in the other two systems. This result can be explained by an increase in the electronegativity in the order Ba < K < Mg.

3.2. EPR study

As can be seen in figures 2 and 3, each EPR spectrum has two principal features. The first is a broad asymmetric band at low magnetic field with an effective g value of $\sim$5. The second is a broad and asymmetric line at high magnetic field with an effective g value of $\sim$1.9 (table 3). In all spectra, the low-magnetic-field signal presents a smaller shoulder situated at $g = 4.6$. Except for the variation in signal intensity no important modification was observed when increasing the temperature or concentration (figures 2 and 3). A slight shift in the resonance signals was also observed when modifying the starting glass composition.

The EPR spectra of glasses are usually interpreted on the basis of a spin Hamiltonian and a powder pattern. The free Cr^{3+} ion, with its three unpaired electrons and total spin $S = 3/2$ is in the ^4F ground state. Within an octahedral crystal field, this state splits into an orbital singlet $^4A_{2g}$ and two orbital triplets $^4T_{1g}$ and $^4T_{2g}$ [15]. However, Cr^{3+} ions are usually considered in distorted octahedral sites and their electronic levels can be described

Table 3. Effective *g* values for the different phosphate glass systems.

Glass system	Effective *g* values
PBa [15]	4.92, 1.97
PBaK [This work]	5.12, 4.52, 1.99
PBaKMg [This work]	5.20, 4.43, 1.89

by a spin Hamiltonian of the form [21]:

$$H_s = g\beta HS + D\left[S_z^2 - \tfrac{1}{3}S(S+1)\right] + E(S_x^2 - S_y^2) \tag{1}$$

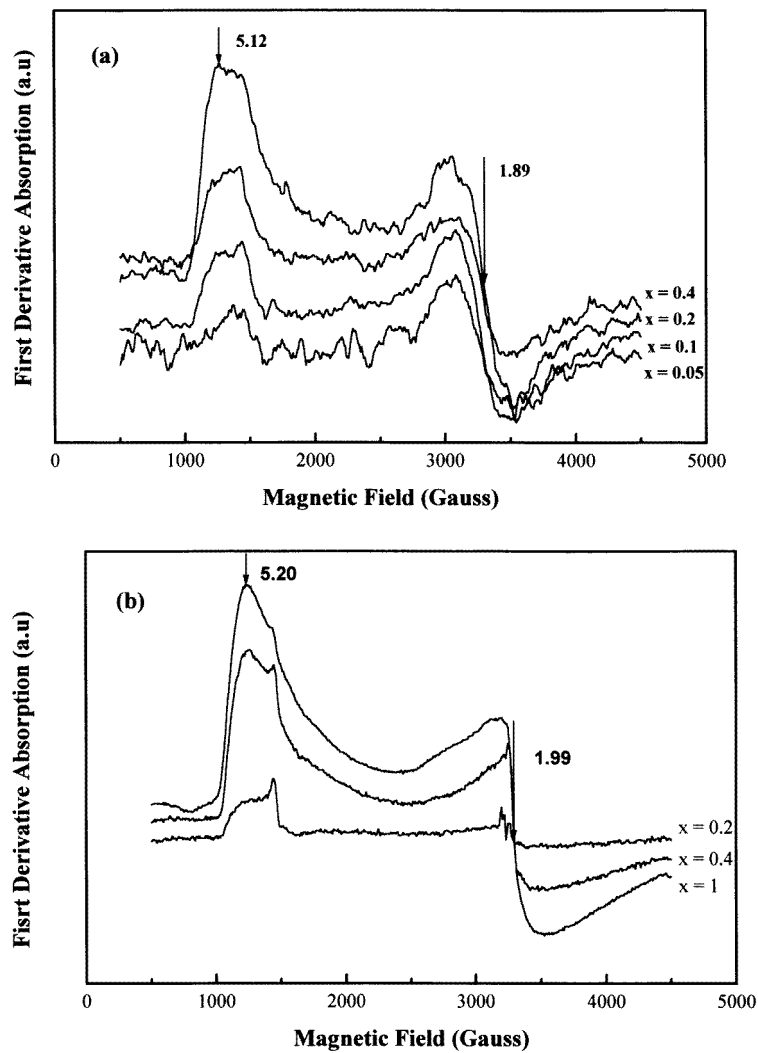where the terms involving D and E are the axial and orthorhombic crystal-field components,

Figure 2. 100 K EPR spectra of the Cr³⁺-doped phosphate glasses: (a) for the PBaK and (b) for the PBaKMg glass systems.
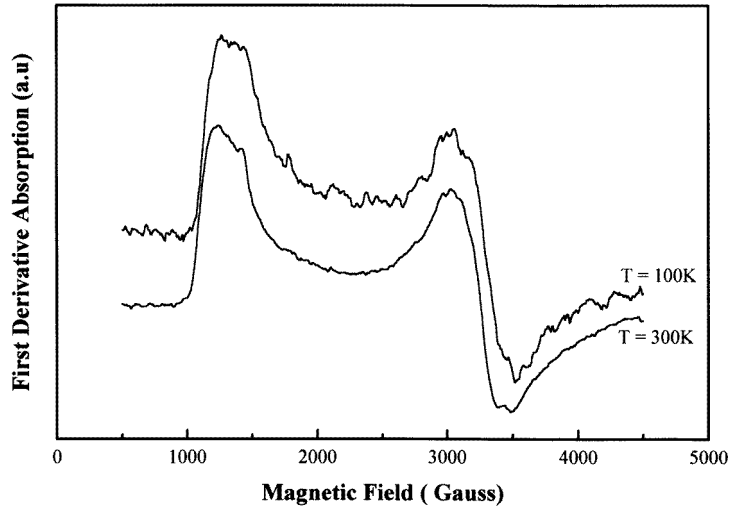
Figure 3. EPR spectra for the PBaK glass system ($x = 0.1$) at 100 and 300 K.

respectively, S is the spin operator and g is the gyromagnetic tensor. In the absence of an external magnetic field H, the four-spin degeneracy of the $^4A_{2g}$ state is removed by a subsequent low symmetric field and we have a zero-field splitting of the Kramer doublets $|\pm3/2\rangle$ and $|\pm1/2\rangle$ separated by an energy $\Delta_{zfs} = 2(D^2 + 3E^2)^{1/2}$. In the presence of a magnetic field, the degenerate doublets split further. When applying an rf field, a transition with $\Delta ms = \pm1$ may be observed in the EPR spectra. However, the number of bands depends upon the magnitude of the zero-field splitting for a given rf photon energy [21, 22].

To account better for the features observed in the EPR spectra of Cr^{3+}-doped glasses at $g_{eff} = 5.0$ and $g_{eff} = 1.78$, Zakharov and Yudin [23] exactly diagonalized the fine-structure perturbation term of equation (1), allowing E/D to take any value. They attributed the observed signals to transitions between the perturbed states stemming from the Kramer ones. In his discussion of the results of these authors, Griscom [24] suggested a distribution of $\xi = |E/D|$ which qualitatively accounts for the observed spectra. Legein *et al* [25] studied the EPR of Cr^{3+} in fluoride glasses and found spectra which are quite similar to those observed by us. By the use of a spin Hamiltonian of the form (1), and a continuous fine-structure distribution of crystal-field parameters, they were able to reconstruct the observed EPR spectra of several transition-metal ions in glasses. They suggested that Cr^{3+} ions occupy nearly octahedral sites. We also attribute the observed spectra to Cr^{3+} ions at nearly octahedral sites with a large zero-field splitting compared with the rf photon energy [21, 22]. The low-magnetic-field resonance signal at $g \sim 5$ is generally attributed to isolated Cr^{3+} ions in distorted sites ($\Delta_{zfs} > h\nu$) while the resonance signal at $g \sim 2$ is usually associated with the contribution of both exchange-coupled Cr^{3+}–Cr^{3+} pairs and isolated Cr^{3+} ions [26]. However, the intensity of this signal decreases with increasing temperature (figure 3). In contrast to our observation, the calculations of Fournier *et al* [27] show that the intensity of the resonance signal at $g \sim 2$ increases with increasing temperature if exchange is important. Consequently, we attribute this signal essentially to isolated Cr^{3+} ions. The signal which appears in the low-magnetic-field region at $g \sim 4.6$ is attributed to Fe^{3+} ion impurities in the raw materials used in the preparation of the glasses as seen in [22,

28]. The large line widths observed in EPR spectra are due to the random variation of crystal-field parameters in contrast with crystallite systems which do not exhibit the broad feature at $g \sim 5$ typically seen in glasses. Knutson *et al* [22] showed that resonance can be obtained within a large domain of magnetic field because of the great disorder and the large distribution of crystal-field parameters from site to site which induce a spreading of the spectrum and broadening of the resonance lines. From this study, we also conclude that Cr^{3+} ions have approximately the same environment in the two glass systems: PBaK and PBaKMg. This result is supported by the similarity of the EPR spectra observed for those glasses.

Both optical absorption and EPR data can also confirm the preceding results. In fact, it can be shown [15] that the effective g factor for a transition-metal ion is proportional to g_0 where

$$g_0 = g_e - \frac{8\alpha\lambda}{\Delta}. \tag{2}$$

Here g_e is the free electron g factor ($g_e = 2.0023$), λ is the spin–orbit coupling constant, Δ is the energy difference between the ground and the excited electronic levels. The parameter α is characteristic of the ionic contribution to the chemical bond between the Cr^{3+} ion and the ligands. The larger the value of α, the stronger the ionic contribution to the chemical bond and the smaller the value of the g factor. The g values found in this work (table 3) confirm that the ionic contribution to the chemical bond is less important in the PBaKMg glass than in the PBaK systems. This result is also explained by a decrease of the electronegativity from Ba to Mg [15, 16].

4. Conclusion

From optical absorption and EPR studies, we can conclude that Cr^{3+} ions are located in sites with nearly octahedral symmetry in both PBaK and PBaKMg glass systems but that the crystal-field strength increases in the order: PBa < PBaK < PBaKMg. The EPR spectra indicate that the zero-field splitting is relatively large compared with the X-band photon energy. The chemical bond between the Cr^{3+} ions and the ligands is rather covalent in character. The PBaKMg glass system seems to be more important than the PBaK one for efficient optical pumping because of its transparency in the high-energy region.

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