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Spectroscopic studies on Pb_3O_4–ZnO–P_2O_5 glasses doped with transition metal ions

G. Giridhar [a], S. Sreehari Sastry [b,*], M. Rangacharyulu [b]

[a] Department of Nanotechnology, Acharya Nagarjuna University, Centralised Lab road, Nagarjuna Nagar 522510, Andhra Pradesh, India
[b] Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar 522510, Andhra Pradesh, India

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ABSTRACT

Optical absorption, Electron Paramagnetic Resonance (EPR) studies are carried out on lead zinc phosphate glass systems doped with Cr^{3+} and VO^{2+}. From optical absorption investigations the crystal-field parameters Dq, *B* and *C* are evaluated. EPR measurements on Cr^{3+} systems indicate that Cr^{3+} ions are located at sites with low symmetry. EPR spectra of vanadyl doped system revealed the characteristic nature of vanadyl ion. Spin-Hamiltonian and hyperfine values are evaluated for both the systems. Optical absorption spectra of vanadyl doped system revealed three bands that are characteristic of VO(II) ion in tetragonally distorted octahedral site. By correlating both EPR and optical data, the dipolar coupling constant (P) and Fermi-constant coupling parameter (κ) and molecular orbital coefficients β^{*2}, e_π^{*2} are evaluated. Electron Paramagnetic Resonance and optical absorption studies showed that the chemical bonds of Cr^{3+} ions and VO^{2+} ions with the ligands have more covalent nature. From these studies it is also observed that lead spinals are playing major key role in sustaining the covalent nature of bonding.

1. Introduction

Glasses with large non-linear refractive index and non-linear absorption coefficient are used for fiber optic communication and for fabrication of non-linear optical devices [1]. So, there is good demand for glasses with high optical non-linearity and higher damage resistance at reduced cost. Phosphate glasses have attracted considerable attention in recent years due to their nonlinear optical properties. Considerable work had been done on lead zinc phosphate glasses because of their low melting nature [2–7]. Earlier workers conducted optical studies on lead zinc borate glasses [8] and noticed a long infrared cutoff as a property that shows their usefulness in many potential applications. In continuation [9–11] our work deals with phosphate glasses doped with transition metal ions and rare earth ions with lead spinals. The present work deals with the chromium and vanadyl as dopants in lead zinc phosphate glasses and these systems are investigated using Electron Paramagnetic Resonance and optical absorption techniques. An attempt is made to determine the microscopic insight of glasses that leads to development of glasses suitable for different nonlinear optical applications.

2. Experimental

The materials used in the present study are Analar grade Pb_3O_4, ZnO, Cr_2O_3 and P_2O_5. The host glass composition is taken as 10 Pb_3O_4 + 30 ZnO + 59.9 P_2O_5 + 0.1 Cr_2O_3 and 10 Pb_3O_4 + 30 ZnO + 59.9 P_2O_5 + 0.1 V_2O_5. For each concentration, the mixture is first sintered at 700 K after thoroughly mixing it using the quench melting method. The resulting sample is kept in a porcelain crucible and then it is melted in an electric furnace at 1200 K for nearly 1 h. Glass is formed by quenching the melt at room temperature in air. Then the formed glass is annealed at 550 K for 30 min. To ensure the amorphous nature of the glass, X-ray diffraction studies are performed through PHILIPS X'PERT PRO X-RAY diffraction system. EPR spectra are recorded at room temperature through a JES-FA series X-band EPR spectrometer having 100 kHz field modulation. Optical absorption spectra of these glasses are recorded at room temperature through JASCO (V-530) spectrophotometer in UV–visible region.

3. Results and discussion

No sharp peaks are exhibited in powder X-ray diffraction spectra of Cr^{3+} and VO^{2+} doped lead zinc phosphate glass samples, and it is concluded that the samples are amorphous in nature.

3.1. Chromium doped glass

The optical absorption spectra for the Cr^{3+} doped lead zinc phosphate glass is shown in Fig. 1. The low-energy band in the

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[*] Corresponding author. Tel./fax: +91 863 2293674.
E-mail address: sreehari_ssastry@yahoo.com (S. Sreehari Sastry).

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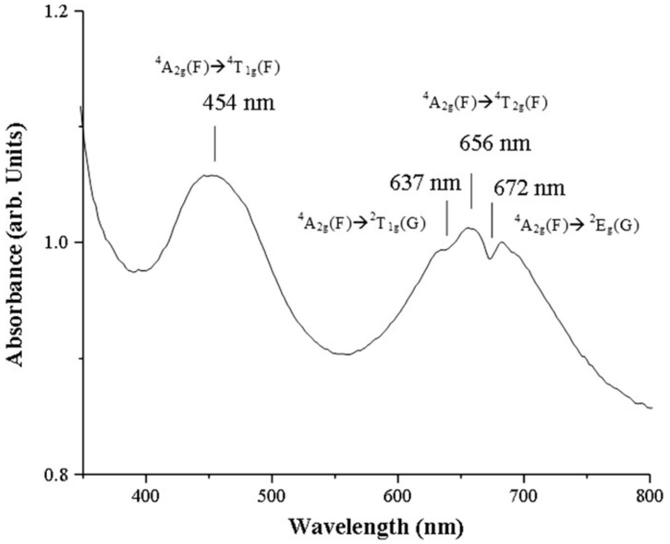

Fig. 1. Optical absorption spectra of chromium doped lead zinc phosphate glass.

Table 1
Assignment of band position for corresponding electronic transition.

Electronic transition	Band position (cm^{-1})	
	Experimental	Calculated
$^4A_{2g}(F)\rightarrow{}^2E_g(G)$	14863.6	14912.2
$^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ (v_1)	15228	15220
$^4A_{2g}(F)\rightarrow{}^2T_{1g}(G)$	15699.2	15553.8
$^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ (v_2)	22020.4	22019.8

optical spectrum shows fine structure. By the crystal field theory, Cr^{3+} ions are usually assumed to occupy approximately octahedral symmetry sites in inorganic solids. This is due to the strong ligand field stabilization energy of Cr^{3+} ions in six-fold coordination. The parity-forbidden d–d transitions observed may be due to the weak distortion of the crystal field or by instantaneous distortion due to molecular vibrations [12–14]. The Cr^{3+} ions in octahedral symmetry are characterized by three spin-allowed transitions $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$, $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$. In the present case only the first two transitions are observed. In the profile of $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$, it is well known that the spectrum of Cr^{3+} doped glasses exhibits two dips [15]. These dips are due to the Fano anti-resonances resulting from the interaction of the $^2T_{1g}(G)$ and $^2E_g(G)$ with vibrationally broadened $^4T_{2g}$ (F) state [16]. Band assignment of the optical spectra supposing Cr^{3+} ions to be located at nearly octahedral sites are also shown in Table 1.

On the basis of these band assignment v_1 the crystal field parameter Dq is evaluated as 10Dq. The Racah inter-electronic repulsion parameter B can be evaluated from

$$B=\frac{2v_1^2+v_2^2-3v_1v_2}{15v_2-27v_1}$$

here v_1 and v_2 represent the energies of $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$, respectively. Racah's 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. Based on the above assignments the energy matrices of d^3 configuration are solved for different values of crystal field (Dq) and inter electronic repulsion (B and C) parameters. The value of C is evaluated using the relation given by Rasheed et al. [17]:

$$\frac{C}{B}=\frac{1}{3.05}\left[\frac{E(^2E)}{B}-7.9+1.8\left(\frac{B}{\text{Dq}}\right)\right]$$

A good fit with the experimental results is obtained. The calculated bands are also presented in Table 2. The value of B is a measure of inter-electronic repulsion in the d-shell and is useful in determining the ionic/covalent properties of Cr^{3+} ligand bonding and is shown in Table 2.

The measured value of B by both the methods is ~710 cm^{-1}, which is lower than the $B_{\text{free}}=1030$ cm^{-1} [18] value of the free Cr^{3+} ion. Bonding can also be evaluated using the Seeber et al. formula [19]:

$$h=\frac{[(B_{\text{free}}-B)/B_{\text{free}}]}{k_{\text{Cr}^{3+}}}$$

where h and k are nephelauxetic functions of the ligands and the central metal ion. Racha parameter B and nephelauxetic relation (B/B_{free}) is a measure of bond of covalency ligand-dopant. The covalency increases when the values of B and (B/B_{free}) are reduced [19–22]. For Cr^{3+} ion, the value of $k=0.21$ [19,23]. The larger value of h means an increased delocalization of d-electrons due to d orbitals overlapping with ligand orbitals. In the present study h value is 1.479, which suggests the increase in covalent bonding nature between Cr^{3+} and the ligands.

From the EPR spectra shown in Fig. 2, Cr^{3+} doped lead zinc phosphate glass exhibited two resonance signals at $g=4.6255$ and 1.9993. Both the signals are broad and asymmetric at low and high magnetic fields. The larger line widths observed in the EPR spectra are due to the random variation of crystal field parameters at various sites. Crystalline systems do not exhibit the broad feature.

Table 2
Inter-electronic repulsion parameters.

Parameters	Experimental (cm^{-1})	Calculated (cm^{-1})
Dq	1522.8	1522
B	708.6	710
C	3232.48	3250

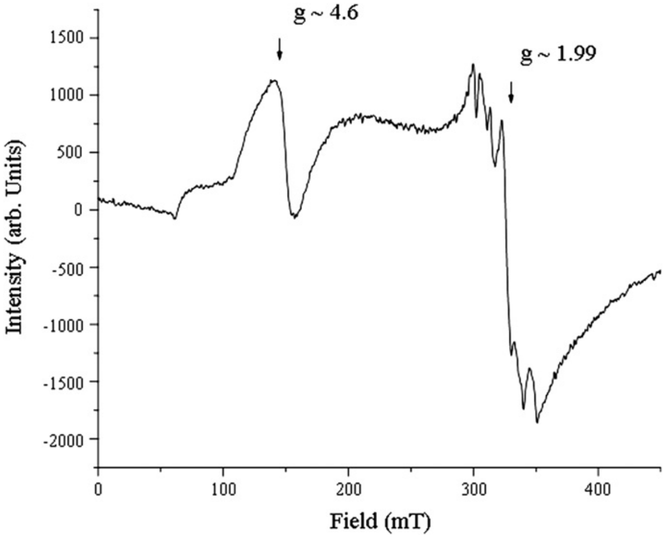

Fig. 2. Electron Paramagnetic Spectrum of chromium doped lead zinc phosphate glass at X-band frequency.