

Structural Investigations of Cr³⁺ Ions Doped Alkali Lead Zinc Phosphate Glasses

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ABSTRACT: Lead zinc phosphate glasses containing 0.1% transition metal ion Cr³⁺ were prepared by melt quenching technique and their amorphous nature confirmed by X-Ray diffraction. The covalent bond nature of Cr³⁺ ions with octahedral symmetry in glass network was established through Electron Paramagnetic Resonance and optical absorption spectroscopic studies. Endothermic dip for glass transition temperature (T_g) at about 410 °C and an exothermic peak subsisted from thermal studies were obtained. De-polymerization of host glass network due to addition of alkali content to the glass matrix, has turned as a strong candidate for nonlinear optical laser applications.

KEYWORDS: Amorphous materials; Electron Paramagnetic Resonance; Optical spectroscopy; Lead Zinc Phosphate glass; Ligand field theory.

I. INTRODUCTION

Phosphate glasses are important materials in scientific and technological aspects due to their structural versatility in accepting several cation and/or anion exchanges. These features that extend scope for re-engineering of glass formulation will influence their physical properties. In addition, several glass systems possess a great potential for application to second-order and third-order nonlinear optical, electro-chromic, photochromic and thermochromic devices [1–12]. Among oxide glasses, the phosphate glasses are particularly attractive hosts because they can accommodate large concentrations of active ions without losing the useful properties of the material. There is a good demand for glasses for their high optical non-linearity and higher damage resistance properties available at reduced cost. Phosphate glasses are stable as electrochemically and thermally with good ionic conductivity. Hence, these glasses find applications in construction of solid state ionic devices, photonic materials and biomedical materials [13–15]. Considerable work had been done in recent years on lead zinc phosphate glasses due to their nonlinear optical properties and low melting nature [16–21].

Transition Metal ions (TM) are the simplest and most well suited for applications due to a partially filled *d*-shell. The glasses' optical absorption studies shed light on ligand field absorption energies that are sensitively to reflect distortion of the cubic, octahedral and tetrahedral co-ordinations. Cr³⁺ is interesting in TM ions, because of being extreme sensitivity in optical spectra to the nature of the host matrix. Hence, Cr³⁺ is a very useful probe to obtain information about an amorphous local environment in the glasses [22]. Even though, the previous spectroscopic results of Cr³⁺ in Pb₃O₄-ZnO-P₂O₅ glass matrix indicated as nearly octahedral site symmetry for Cr³⁺, the detailed studies on the structure and properties of phosphate glasses have been rather limited due to hygroscopic behaviour and volatility of P₂O₅ at elevated temperatures [23]. The work aims to characterizing Pb₃O₄-M₂O-ZnO-P₂O₅ (where M=Li, Na and K) glasses (hereafter referred to as LPZ, NPZ and KPZ glasses) doped with Cr³⁺ by using EPR and optical absorption spectroscopic studies and to understanding bonding mechanism and Pb (IV-II) apportionment in the company of different alkaline metals that are resulted out due to variation of optical band gap energy.

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Vol. 4, Issue 3, March 2015

II. EXPERIMENTAL

The materials used in the present study are 99.9% analar grade Pb_3O_4 , ZnO , Cr_2O_3 , Na_2CO_3 , Li_2CO_3 , K_2CO_3 and P_2O_5 . The host glass composition is taken as

10 Pb_3O_4 + 20 Li_2O + 10 ZnO + 59.9 P_2O_5 + 0.1 Cr_2O_3 (LPZ Glass)

10 Pb_3O_4 + 20 Na_2O + 10 ZnO + 59.9 P_2O_5 + 0.1 Cr_2O_3 (NPZ Glass)

10 Pb_3O_4 + 20 K_2O + 10 ZnO + 59.9 P_2O_5 + 0.1 Cr_2O_3 (KPZ Glass)

For each concentration, the mixture is first sintered at 425 °C by using the quench melting method after thoroughly mixing it. Then the sample is kept in a porcelain crucible and melted in an electric furnace at 925 °C for nearly one hour. The crucibles are shaken frequently to achieve homogeneous mixing of all the constituents. The melt is quenched at room temperature in air by pouring between two brass plates. The formed glasses are annealed at 275 °C for 30 minutes from protecting the sample to break due to residual internal strain. The developed light green coloured glasses are then cut into proper shapes for further characterization.

To ensure amorphous nature of the glass, X-ray diffraction studies are performed through PHILIPS X'PERT PRO X-RAY diffractometer. Differential scanning calorimetric studies are conducted on samples using TA instruments DSC 2010 system with a ramp rate of 10 °C/min. EPR spectra are recorded at room temperature through 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.

III. RESULTS AND DISCUSSION

The XRD spectrum of the powder of glass system showing amorphous nature of glass is shown as in figure 1.

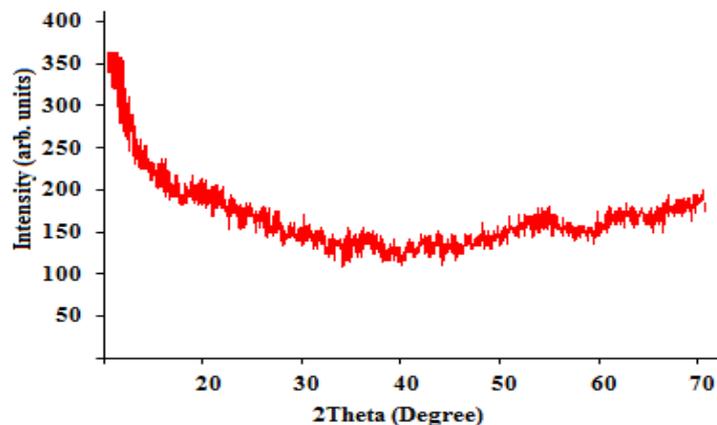


Fig. 1 XRD spectrum of Cr^{3+} ions doped alkali lead zinc phosphate glass

DSC traces are collected over approximately 0.5g of glass powder by heating at 50 °C to 800 °C temperature range maintaining a ramp rate of 10 °C/min. Temperatures are measured to the accuracy of ± 1 °C that are shown in figure 2. Glass transition temperature, T_g , is obtained from figure 2 that is the one corresponding to the minimum dip in heat flow. The endothermic dip occurred at 410 °C, on the DSC curve attributed to the transition of the glass structure. On further increase in temperature, an exothermic peak T_c , which is related to the crystallization of dielectric phases in glass matrix, is recorded at 598 °C with maximum intensity.

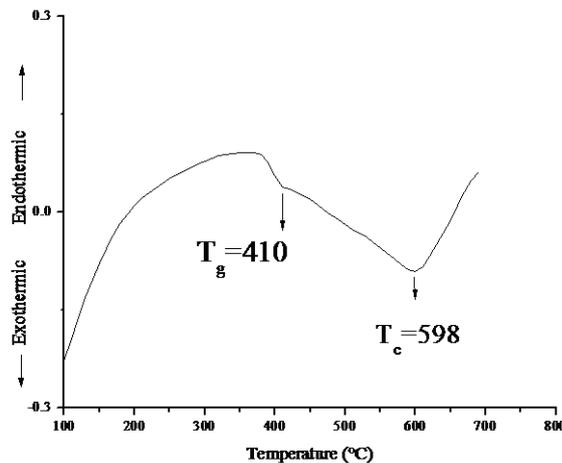


Fig. 2 DSC traces of Cr³⁺ ions doped alkali lead zinc phosphate glass

The optical absorption spectra for prepared (where M = Li, Na and K) glasses are recorded in between 200–900 nm wavelength. Pure glass is colourless with no characteristic bands in both ultraviolet and visible regions. The slow exponential rise of absorption is an indication of indirect transitions of electrons. Using the Tauc equation [24], optical band gap is calculated for these glasses, and absorption coefficient (α) from the expression (1) [25]

$$\alpha = C \frac{(\hbar\omega - E_{opt})^2}{\hbar\omega} \quad (1)$$

where C is constant and α expected to be $> 10^4 \text{ cm}^{-1}$ in the case of direct transitions. However, it is to note that in most of the bulk glasses including the present one α seems to be in the order of $10^2 - 10^3 \text{ cm}^{-1}$ even if the thickness is reduced to a few tens of centimetres. The above equation (1) is still suitable to apply because the absorption edge in disordered materials is usually interpreted in terms of indirect transitions across the optical band gap [25]. Since this equation can be readjusted to represent the linearity between $(\alpha\hbar\omega)^{1/2}$ and $(\hbar\omega - E_{opt})$, following the procedure given by Dayanand *et al* [26], the E_{opt} value is determined from the plot of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ (eV).

The optical absorption spectra for the Cr³⁺ doped lead zinc phosphate glass is shown in figure 3. The low-energy band in the optical spectrum shows fine structure. By the crystal field theory, Cr³⁺ ions are typically implicit to reside in approximately octahedral symmetry sites. On the basis of the band assignment the crystal field parameter D_q is estimated from band position of ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ as $10D_q$. The Racah's inter-electronic repulsion parameter B is derived from equation (2)

$$B = \frac{2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2}{15\nu_2 - 27\nu_1} \quad (2)$$

here ν_1 and ν_2 represent the energies of ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ respectively. The Racah's parameter B is considered as a measure of inter-electronic repulsion in the d-shell. The larger the B value, more are the electrons localized on transition-metal ion. Based on the above assignments the energy matrices of d³ configuration are resolved for different values of crystal field (D_q) and inter electronic repulsion (B and C) parameters. The value of C is derived from the relation (3) given by Rasheed *et al* [27].

$$\frac{C}{B} = \frac{1}{3.05} \left[\frac{E(^2E)}{B} - 7.9 + 1.8 \left(\frac{B}{Dq} \right) \right] \quad (3)$$

The measured value of B by both methods is $\sim 710 \text{ cm}^{-1}$ which is lower than the $B_{free} = 1030 \text{ cm}^{-1}$ [28] value of the free Cr³⁺ ion. The bonding is also estimated from Seeber *et al.* formula (4) [29].

$$h = \frac{[(B_{free} - B) / B_{free}]}{k_{Cr^{3+}}} \quad (4)$$

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 3, March 2015

where h and k are nephelauxetic functions of the ligands and the central metal ion respectively.

Fig. 3 shows that Cr_2O_3 doped glasses attained light green colour and two bands at 450 nm (2.75 eV) and 650 nm (1.9 eV) present in the visible region. The UV cut-off has shifted to lower wavelength about ~ 340 nm (3.65 eV). The spectra indicate the chromium presence in the $3+$ coordination state in alkali lead zinc phosphate glass network. The two visible bands at about ~ 450 nm and 650 nm are referred to presence of Cr^{3+} ions mostly in distorted octahedral coordination. The presence of octahedral sites is due to strong ligand field stabilization energy of Cr^{3+} ions in six-fold coordination. The parity-forbidden $d-d$ transitions may be due to partially allowed by weak distortion of the crystal field or by instantaneous distortion due to molecular vibrations [30-34]. Here, the E_{opt} values are 3.43eV, 2.71eV, 3.39eV and 3.36eV for LPZ glass, NPZ glass, KPZ glass and PZ glass [23] respectively. The higher value of E_{opt} for LPZ glass is attributed to the presence of Pb^{4+} ion in the glass giving rise to $\text{O}-\text{Pb}^{4+}-\text{O}-\text{Pb}^{2+}-\text{O}-\text{Pb}^{2+}$ [35], which is covalent strengthening the glass network by increasing number of bridging oxygen ions. This increase in bridging oxygen is considered [36] as responsible for higher E_{opt} observed in LPZ glass.

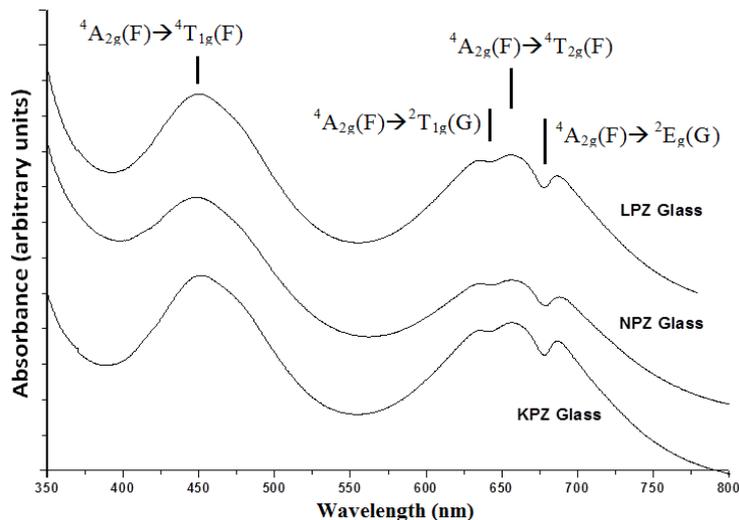


Fig. 3 Optical absorption spectra of Cr^{3+} ions doped alkali lead zinc phosphate glass

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 ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$. However, here in this case, only two bands are recorded for first two transitions. In the profile of ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, the spectrum of Cr^{3+} doped glass will exhibit two dips [37]. These dips are resulted due to Fano anti-resonances from the interaction of the ${}^2T_{1g}(G)$ and ${}^2E_g(G)$ with vibrationally broadened ${}^4T_{2g}(F)$ state [38]. Band assignment of the optical spectra supposing Cr^{3+} ions ideally located at nearly octahedral sites are also shown in Table 1.

Table 1: Assignment of Band position for corresponding electronic transition of Cr^{3+} ions doped alkali lead zinc phosphate glasses

Electronic Transition	Band position (cm^{-1})					
	LPZ Glass		NPZ Glass		KPZ Glass	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
${}^4A_{2g}(F) \rightarrow {}^2E_g(G)$	14738	14741	14714	14718	14736	14766
${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) (\nu_1)$	15193	15190	15172	15170	15216	15210
${}^4A_{2g}(F) \rightarrow {}^2T_{1g}(G)$	15516	15403	15497	15403	15572	15418
${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F) (\nu_2)$	22059	22063	22142	22142	22044	22047

The values of Crystal field parameter D_q and Racah's inter-electronic repulsion parameters B , C are presented in Table 2. These values are good in agreement with the experimental results. The value B is a measure of inter-

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 4, Issue 3, March 2015

electronic repulsion in the d-shell, which is useful in determining the ionic/covalent properties of Cr³⁺ ligand bonding. Racha's parameter *B* and nephelauxetic relation (*B/B_{free}*) is a measure of bond covalency of ligand-dopant. The covalency increases when the values of *B* and (*B/B_{free}*) are reduced [29, 39-41]. For Cr³⁺ ion, the value of *k* is 0.21 [42]. The larger value of *h* means an increased delocalization of *d*-electrons which are resulted out of *d* orbitals overlapping with ligand orbitals. In the present study *h* represents the values 2, 1.89 and 2 which suggest the increase in covalent bonding nature between Cr³⁺ and the ligands.

Table 2: Inter-electronic repulsion parameters for Cr³⁺ ions doped alkali lead zinc phosphate glasses

Glass Sample	Dq in cm ⁻¹		B in cm ⁻¹		C in cm ⁻¹		Dq/B
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	
LPZ Glass	1519.3	1519	721	722	3208	3170	2.1
NPZ Glass	1517.2	1517	738	738	3174	3130	2.0
KPZ Glass	1521.6	1521	714	716	3221	3190	2.1

The EPR spectra in fig. 4 is indicating Cr³⁺ doped lead zinc phosphate glasses exhibiting two resonance signals at *g* ~ 4.8 and *g* ~ 1.97, which are tabulated in Table 3. Both these signals are broad and asymmetric at low and high magnetic fields respectively. The optical and EPR data as well have confirmed the preceding results. In fact, it can be shown [43] that the effective *g* factor for a transition metal ion is proportional to *g*₀ as per the equation (5)

$$g_0 = g_e - \frac{8\alpha\lambda}{\Delta} \tag{5}$$

where *g_e* is the free electron *g* factor (*g_e* = 2.0023), *λ* for the spin-orbit coupling constant (91 cm⁻¹ for Cr³⁺ ions), *Δ* for the energy difference between the ground and the excited electronic levels.

The larger line widths occurred in Fig. 4 are caused by variation of crystal field parameters at various sites. Crystalline systems do not exhibit the broad feature. In the presence of the low symmetry component, the *g* value near to 2.0 is assigned to exchange coupled Cr³⁺ ions based on Haouari *et al.*'s assignments [33] and on Ardelean *et al* [44], that explain the existence of Cr⁵⁺ for lower concentrations of Cr₂O₃ [45, 46]. The signal that appears in the low magnetic field region at *g* ~ 4.8 is attributed to Fe³⁺ ion impurities in the raw materials used in the preparation of the glass [44]. Hence, it is concluded in this study that Cr³⁺ ions have distorted octahedral environments. The *g*-values and bonding parameter values obtained from EPR and optical absorption studies have indicated that the prepared glasses are covalent in nature. The results of both *g*-values and bonding parameter values drawn from the EPR and optical absorption studies have clearly indicated the covalent nature. The parameter *α* = 0.67, 0.62 and 0.66, estimated from the above relation (5) is characteristic of the ionic contribution to the chemical bond between the Cr³⁺ ion and the ligands. The larger the value of *α*, the stronger is the ionic contribution to the chemical bond and also the smaller the value of the *g* factor. But here, contrary the ionic contribution parameter is lower and *g* value is high. These results have supported that the chromium doped system which has the metal- ligand linkage is of more covalent nature. The *E_{opt}* value for LPZ glass is 3.43 eV, which is more than other glasses as 2.71eV, 3.39eV for NPZ and KPZ glasses respectively. From the results LPZ glass has more covalent nature when compared to others due to the

Table 3: Experimental *g*- values at higher and lower magnetic fields of Cr³⁺ doped alkali lead zinc phosphate glasses

Glass Sample	<i>g</i> – values	
	Higher	Lower
LPZ Glass	1.9703	4.84
NPZ Glass	1.9724	4.86
KPZ Glass	1.9707	4.92

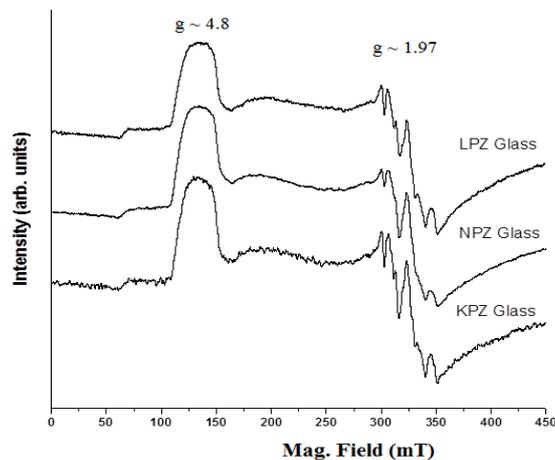


Fig. 4 EPR spectra of Cr³⁺ ions doped alkali lead zinc phosphate glasses

presence of Pb⁴⁺, which develops the bridging oxygens as mentioned by earlier work [23, 35]. Therefore two states of Pb₃O₄ as Pb²⁺ and Pb⁴⁺ (2PbO + PbO₂) are the major assets in increasing the lead concentration. When PbO enters the network, it is expected to form PbO₄ units in which lead is coordinated to four oxygens in a covalently bonded configuration. It is anticipated that lead will not reside in the glass network interstitially. For a constant content of P₂O₅ the substitution of ZnO by PbO leads to an increase in the network disorder.

The changes in network structure, bonding nature, high amorphous character and to increasing optical behaviour used to occur not only due to the presence of Pb⁴⁺ but also alkali content, which is helpful in depolymerization of phosphate network. Lithium, acting as modifier, is more effective than sodium and potassium in breaking the phosphate network because of its low ionic radius (Li < Na < K) and high electronegativity (Li > Na > K). Hence, it is unambiguous that the bridging oxygens caused by Pb⁴⁺ will develop Pb²⁺ - O - Pb⁴⁺ - O - Pb²⁺ and Pb-O-Zn chains linking the phosphate tetrahedral in a covalent bond configuration. The present spectroscopic studies also confirmed the same observation and indicated the decrease in network connectivity for this alkali lead zinc phosphate glass system. For g ~ 1.9, the glasses are more efficient for optical pumping because of its transparency in the high energy region and same is also revealed by D_q/B for its high value for LPZ glass. This increases the crystal field strength causing the high band gap energy for the proposed glass. When a metal-oxygen bond is broken, the bond energy is released. The non-bonding orbitals have higher energies than bonding orbitals. Because of Pb⁴⁺, the increase in the bridging oxygens results in shifting of valence band minimum [consists of O(2p) orbitals] to lower energies, and increasing the band gap. As lead partially participates in the network formation [46] and decompose into nano scale separated entities, these entities account for higher optical properties [43, 47] for LPZ glass sample. Lead phosphate glasses possess enhanced optical non-linearity due to the high polarizability of Pb²⁺ ions in glass matrices. Electrostatic interaction between transition metal ions and the highly excited Pb⁴⁺ ions is also known to cause this result [48].

IV. CONCLUSIONS

Cr³⁺ ions are located in sites with nearly octahedral symmetry in the present glass systems. The sample exhibits resonance signal at g ~ 2.0 due to exchanged coupled Cr³⁺ ions. Four characteristic bands for Cr³⁺ ions are assigned from the optical absorption spectrum. From these bands, the inter-electronic repulsion and crystal field parameters are evaluated, which support the Covalence nature of the bonding. The higher value of E_{opt} for LPZ glass is attributed to the presence of Pb⁴⁺ ion in the glass giving rise to developing O - Pb⁴⁺ - O - Pb²⁺ - O - Pb²⁺. Lithium is more effective than sodium and potassium in breaking the phosphate network because of its low ionic radius (Li < Na < K) and high electronegativity (Li > Na > K) and acts as a modifier. Further, it is noticed that the lead spinals play a key role in the present glass network due to its structure and developing Pb²⁺ - O - Pb⁴⁺ - O - Pb²⁺ and Pb-O-Zn chains with phosphate tetrahedra. The presence of heavy metal oxide combinations causes the occupation of most of the volume of the network to improve the optical nature of the glass and durability.

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Vol. 4, Issue 3, March 2015

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