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Spectroscopic and Physical Properties of Mn^{2+} spin probe in RO-P_2O_5-ZnO-Pb_3O_4 (R=Li, Na and K) Glasses

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ABSTRACT

RO-P_2O_5-ZnO-Pb_3O_4 (R=Li, Na and K) glasses containing 0.1concentrations of MnO have been prepared. The structural, optical and physical properties of prepared glasses are studied by XRD, UV-Visible, EPR and FTIR techniques. The nature of local symmetry and structural information of the neighboring atoms of dopant ions (Mn^{2+}) in the host matrix have been understood by evaluating the crystal field strength (Dq) and Racah (B & C) parameters. The combined analysis of optical absorption and EPR spectroscopy has indicated that the manganese ions exist in Mn^{2+} (in octahedral) local coordination sites. FTIR results showed that PO_4 are the main structural unit of the glass system and the manganese ions are located in the glass matrix network.

***Keywords* -** Optical glasses, Amorphous nature, EPR and FTIR.

I. INTRODUCTION

Spectroscopic studies are a potent experimental techniques used to understand the microscopic properties of glass such as information about the glassy network and to identify the site symmetry around the transition metal ion. Phosphate glasses have been studied quite a long back [1, 2]. Despite P_2O_5 being a very good glass former unlike TeO_2, B_2O_3, GeO_2 and SiO_2 but these glasses were not considered to have any useful applications due to its hygroscopic nature and high volatility. But with the addition of certain metal oxides like PbO superior physical and chemical properties of the phosphate glasses can be obtained [3, 4]. High ultra-violet and far infrared transmission [5], low melting and softening temperatures, make these glasses potential candidates for many technologically applications, such as medical use and sealing materials [6]. Phosphate glasses are of great attraction as they can accommodate large concentrations of active ions without losing the useful properties of the material. Phosphate glasses due to their high ionic conductivity and much stability as electrochemically and thermally they are employed in the construction of solid state ionic devices, photonic materials and biomedical materials [7-9].

Recently lead zinc phosphate glasses have been investigated due to their nonlinear optical properties and low melting temperature [10-15]. Manganese ions are being used as paramagnetic probes to investigate the structure and properties of various vitreous systems, as manganese ions have a strong demeanour on the magnetic and optical properties of the glass. A great number of interesting studies are accessible on the environment of manganese ion in various inorganic glass systems [16, 17]. Lead phosphate glass systems containing manganese ions are used as paramagnetic probe to study the glass structure and study any favorable solarization reaction of the glass [17]. Mn^{2+} exhibits d^5 configuration which exhibits octahedral nature [18]. The interest in inorganic glasses containing transition metal ions has grown because these glasses have properties of technological importance in electronic, tunable solid state lasers and fiber optic communication systems [19]. Spectroscopic techniques made to obtain information on some of the structural and dynamic phenomenon of a material; and to identify the site symmetry around the transition metal (TM) ions in glasses. The aim of the present work is to study the structural phenomenon and properties of the glasses by means of XRD, UV-Visible, EPR, FTIR spectroscopic measurements.

II. EXPERIMENTAL STUDIES

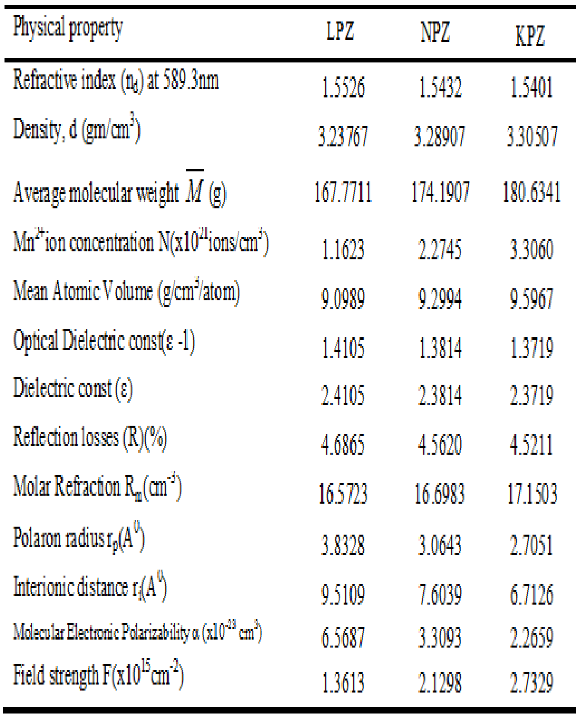
The Mn doped glasses were prepared by using sudden melt quenching technique. The composition of the glass samples used in the present work is presented in Table 1. The chemicals used for the preparation of the present glasses were analar in grade with 99.99% purity. The chemicals are weighed accurately using an electrical balance with accuracy up to fourth digit. Each batch of sample was grounded to a fine powder and thoroughly mixed. The batches were melted at 900°C in a silica crucible in a programmable electrical furnace for 1 hour. The melts were then poured on to a preheated polished brass plate and quickly pressed with another plate. The obtained glasses were annealed at 400°C for 1hr in order to remove thermal strains. The glasses thus obtained are in circular in shape with a uniform thickness 0.2 cm and having a diameter of the order 1–3 cm. The obtained glasses were polished before taking optical measurements.

Table 1: Composition of glasses (mol %) studied in the present work

Glass	Pb_3O_4	RO	ZnO	P_2O_5	MnO
LPZ (R=Li)	10	20	10	59.9	0.1
NPZ (R=Na)	10	20	10	59.9	0.1
KPZ (R=K)	10	20	10	59.9	0.1

The refractive index of the glasses have been measured on Abbe Refractometer (λ = 5893A°) with monobromonapthalane as a contact layer between the sample and prism of a refractometer. The densities of the glasses were measured by using Archimedes principle, with Xylene as an immersion liquid. The various physical properties of the prepared glasses are evaluated by using the standard formulae [20] and are illustrated in Table 2.

Table 2: Various physical properties of Mn^{2+} doped Alkali Lead Zinc Phosphate glasses



Physical property	LPZ	NPZ	KPZ
Refractive index (n_d) at 589.3nm	1.5526	1.5432	1.5401
Density, d (gm/cm^3)	3.23767	3.28907	3.30507
Average molecular weight $\overline{M}$ (g)	167.7711	174.1907	180.6341
Mn^{2+} ion concentration N($x10^{21}$ions/cm^3)	1.1623	2.2745	3.3060
Mean Atomic Volume (g/cm^3/atom)	9.0989	9.2994	9.5967
Optical Dielectric const(ε -1)	1.4105	1.3814	1.3719
Dielectric const (ε)	2.4105	2.3814	2.3719
Reflection losses (R)(%)	4.6865	4.5620	4.5211
Molar Refraction R_m(cm^{-3})	16.5723	16.6983	17.1503
Polaron radius r_p(A^0)	3.8328	3.0643	2.7051
Interionic distance r_i(A^0)	9.5109	7.6039	6.7126
Molecular Electronic Polarizability α ($x10^{-23}$ cm^3)	6.5687	3.3093	2.2659
Field strength F($x10^{15}cm^{-2}$)	1.3613	2.1298	2.7329

To confirm the amorphous nature of the glass powder X-ray diffraction spectra for an undoped glass at room temperature using Cu Kα radiation in the θ-2θ configuration was recorded. The electron paramagnetic resonance (EPR) measurements were performed at room temperature using EPR spectrometer (JES-FA series) operating in X band frequencies (9.205 GHz) with a modulation frequency of 100 KHz. The magnetic field was scanned from 2200 to 4200 Gauss at a scan rate of 250 G min^{-1}. The powdered glass sample of 100 mg was taken in quartz tube for EPR measurements. Absorption spectrum of Mn doped glass was recorded in the spectral region 300 - 1100 nm using JASCO (V-530) spectrometer. The Infrared spectra of glasses were recorded on SHIMADZU 8201 PC FTIR Spectrophotometer.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of the prepared glass. The amorphous nature of the glass was confirmed by recording powder X-ray diffraction spectra for an undoped glass. The absence of Bragg peaks in XRD spectra confirms the amorphous nature of the prepared glasses.

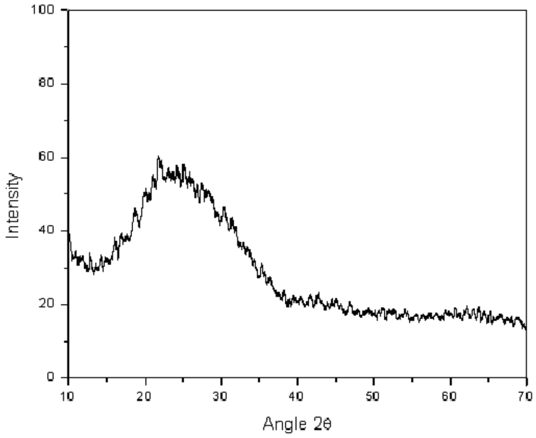


Fig. 1: XRD pattern of Mn^{2+} doped Lead zinc phosphate glass

The EPR spectra of Mn^{2+} doped lead zinc phosphate glass are shown in Fig.2. The EPR spectra of Mn2+ in various glass systems have been studied by many authors [21, 22]. The EPR spectra exhibits an intense resonance signal at around g = 2.0 with six line hyperfine pattern, which is a characteristic of Mn^{2+} ions with a nuclear spin I = 5/2 [23].

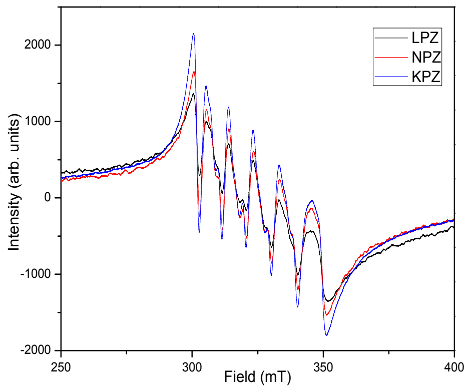


Fig. 2: EPR spectra of Mn^{2+} doped Lead zinc phosphate glasses

The sextet slowly broadened leaving behind a single broad line due to dipole-dipole interaction. The EPR spectra of Mn^{2+}, in general, can be analyzed using the spin-Hamiltonian [24, 25]

$$H=\beta(g_{xx}B_xS_x+g_{yy}B_yS_y+g_{zz}B_zS_z)+(A_{xx}S_xI_x+A_{yy}S_yI_y+A_{zz}B_{zz}I_{zz})+D[S_z^2-(⅓)S(S+1)] + E(S_z^2- S_y^2)$$

where g is the isotropic factor, β is he Bohr magneton, B is the external magnetic field, S is the vector operator of the electron spin momentum and A is the hyperfine interaction parameter, I is the vector operator of nuclear spin momentum and D is the zero field splitting parameter. Investigations of the EPR spectra of Mn^{2+} in a variety of glasses have shown that the spectra have been characterized by an intense resonance signal at around g = 2.0 with six line hyperfine pattern, which is a characteristic of Mn^{2+} ions with a nuclear spin I = 5/2 [24-27].

In case of Mn^{2+} which exhibits d^5 configuration, the axial distortion of octahedral symmetry gives raise to Karmers doublet [28]. The signal at g = 2.0 is due to M_s= |±5/2>, |±3/2> and |±1/2> transition where M_s is effective spin component which is an indication of Mn^{2+} being in octahedral symmetry. The calculated g and A values are shown in Table 3. From Table 3 it is evident that the value of g are approximately same for all glasses, concludes that octahedral symmetry around Mn^{2+} ions is unperturbed by the presence of alkali ion in the glass. If the g-value shows a negative shift with respect to 2.0023, then the bonding is ionic and conversely, if the shift is positive, then the bonding is more covalent in nature. In the present work, from the measured negative shift in the g-value, with respect to 2.0023, it is apparent that the Mn^{2+} ion is in an ionic environment [29]. The measure of covalency between Mn^{2+} ions and its ligands is provided by the magnitude of the hyperfine splitting constant. When the hyperfine splitting constant is large the bonding is more ionic [30]. From the above discussion and by considering the hyperfine splitting constant, it is observed that the Mn^{2+} ions in alkali lead zinc phosphate glasses are quite ionic in nature.

Table 3: The g value and hyperfine splitting constant A value for Mn^{2+} doped Alkali Lead Zinc Phosphate glasses

Glass System	g	A($x10^{-4}$ T)
LPZ	2.009	101.07
NPZ	2.009	100.65
KPZ	2.008	100.08

Optical absorption spectra of Mn^{2+} doped alkali lead zinc phosphate glass are shown in Fig.3. The absorption spectrum shows Mn^{2+} (d^5) can occur in glasses both in tetrahedral and octahedral environments. If the Mn^{2+} are in octahedral symmetry, broad bands are predicted in the visible region (from the ground state $^6A_{1g}(S)$) at about 515 nm (19500 cm^{-1}) from the level, $^4T_{1g}(G)$, and at 445 nm (22500 cm^{-1}) from the level $^4T_{2g}(G)$, and a sharp band at 416 nm (24000 cm^{-1}) from the $^4A_{1g}(G)$, $^4E_g(G)$ levels. If the Mn^{2+} ion is in a tetrahedral symmetry, broad bands are predicted at 442 nm (22650 cm^{-1}) from the $^4T_1(G)$ level, and at 422 nm (23700 cm^{-1}) from the $^4T_2(G)$ level, and at sharp band at 416 nm (24000 cm^{-1}) from the $^4A_1(G)$, $^4E(G)$ levels [31].It can be observed from the spectrum that each glass has exhibited two bands at positions as shown in Table 4.

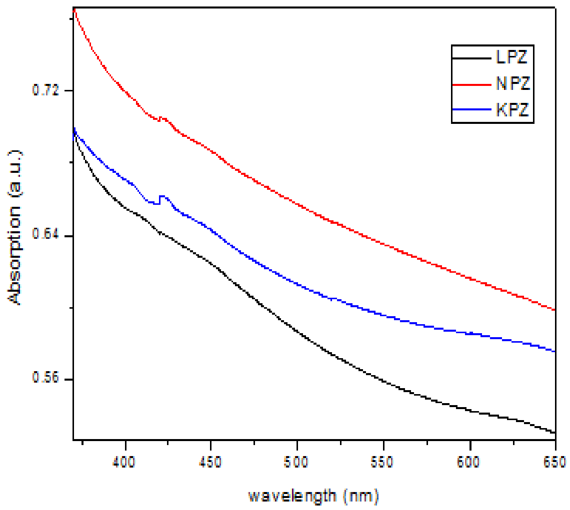


Fig. 3: Optical absorption spectra of Mn^{2+} doped Lead zinc phosphate glasses

Table 4: Optical absorption band positions of Mn^{2+} doped alkali lead zinc phosphate glasses

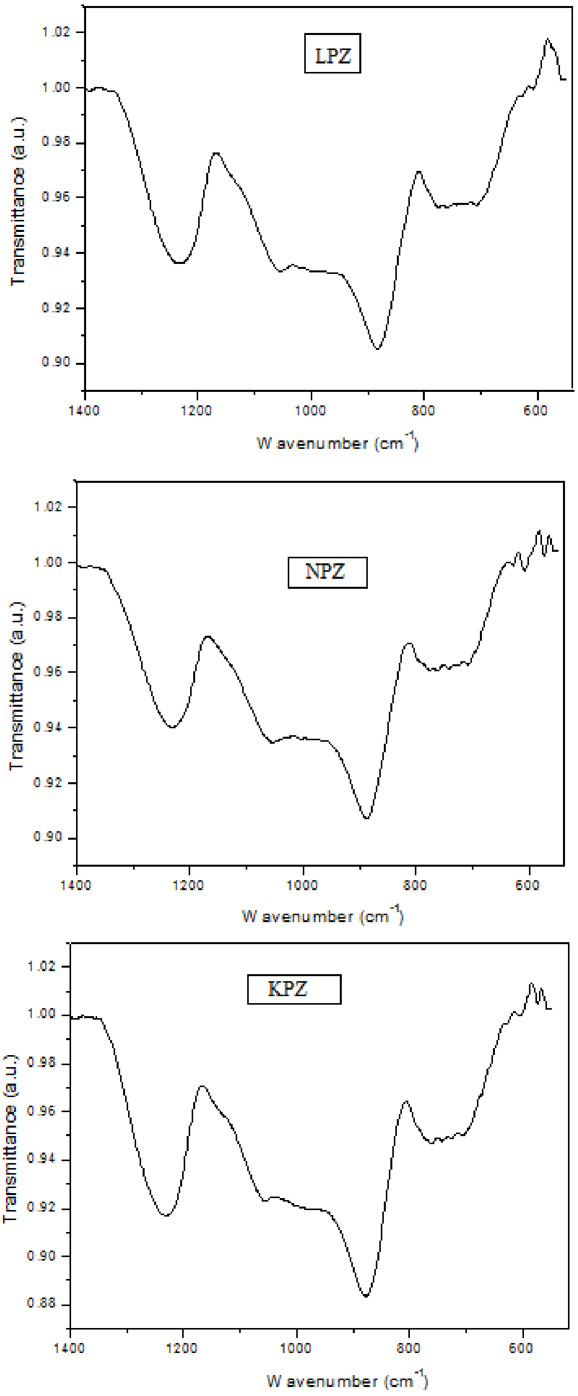
Glass System	Transition $^6A_{1g}(S) \rightarrow$	Observed Wavelength (nm)	Observed Wavenumber (cm^{-1})	Calculated Wavenumber (cm^{-1})
LPZ	$^4T_{2g}(G)$	422	23696	23309
LPZ	$^4A_{1g}(G)+^4E_g(G)$	388	25773	25520
NPZ	$^4T_{2g}(G)$	424	23584	22751
NPZ	$^4A_{1g}(G)+^4E_g(G)$	404	24752	25070
KPZ	$^4T_{2g}(G)$	422	23696	22689
KPZ	$^4A_{1g}(G)+^4E_g(G)$	399	25062	25020

These bands are characteristic of Mn^{2+} in octahedral symmetry. The ligand field bands are sharp, when the energy expressions for the transition are independent of Dq whereas the bands are broad when they depend on Dq. The crystal-field parameter Dq and the inter-electronic repulsion parameters B and C have been evaluated by the energy matrices [32] for the d^5 configuration. In the analysis of the optical spectrum, Trees' correction parameter 'α' = 76 cm^{-1} [33] has also been incorporated to obtain a good fit between the observed and calculated values. The Crystal fields and inter-electronic repulsion parameters are given in Table.5. The deviation of the calculated and observed values also indicates the distorted octahedral environment. The evaluated parameters are in tune with the other reported investigations [25,18]. Thus, the site symmetry around the Mn^{2+} is ascertained to be distorted octahedral.

Table 5: Crystal fields and inter-electronic repulsion parameters of Mn^{2+} doped alkali lead zinc phosphate glasses

Glass System	Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})	A (cm^{-1})
LPZ	810	855	3100	76
NPZ	810	805	3100	76
KPZ	810	800	3100	76

Fig. 4: FTIR spectra of Mn^{2+} doped Lead zinc phosphate glasses



FTIR absorption spectra of glass samples LPZ, NPZ and KPZ are presented in the Fig. 4. The band at about 1280 cm-1 is attributed to $(PO_2)^-$ asymmetrical stretch and/or to P=O stretch [32].

The band observed at ~1080 cm^{-1} is assigned to a normal vibrational mode of PO_4^{3-} group arising out of v_3 − symmetric stretching [33]. The observed strong band in the region 870cm^{-1} in the spectra of all the investigated glasses, which is the characteristic of linear phosphates, suggests the presence of linear chains in them [34]. Another band in the region of 760 - 780 cm^{-1} is due to P–O–P symmetric stretching vibrations. The vibrational modes observed at 600 cm^{-1} for all the glasses are due to the bending mode of the phosphate polyhedra and/or Pb-O and Zn-O vibrations and/or correspond to the Mn–O bond. These shifts can be due to depolymerization process inside glass network. Alkali oxides enter in to the glass network, as a network modifier; and when modifier cations are added to phosphate glasses depolymerization takes place through the breaking of P-O-P linkages and formation of ionic cross bonding between phosphate chains.

IV. CONCLUSION

Amorphous nature of the glass sample has been conformed from its XRD profile. The increase in density for the glass system reveals the change in the structure of the glass with addition of alkali content. The optical absorption spectrum exhibits absorption bands related to characteristic of Mn^{2+} ions in octahedral symmetry. EPR investigations indicated the presence of an isotropic one at g = 2.0 which is due to Mn^{2+} in an environment close to the octahedral symmetry. From EPR and optical spectral studies reveals the nature of the bonding is dominantly ionic and its site symmetry is octahedral. FTIR spectral features indicate a depolymerization process of the phosphate network with successive substitution of alkali content. This implies an increase of the number of NBO’s.

Acknowledgements

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