

Influence of Various Glass Compositions on Physical and Spectroscopic Properties of $\text{CaO-Pb}_3\text{O}_4\text{-ZnO-P}_2\text{O}_5$ Glass System

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ABSTRACT: A series of $20\text{CaO-}10\text{ZnO-}59.9\text{P}_2\text{O}_5\text{-}10\text{Pb}_3\text{O}_4\text{-}0.1x$, ($x= \text{V}_2\text{O}_5, \text{Cr}_2\text{O}_3, \text{MnO}$ and CuO) glasses was prepared by melt quench technique. Spectroscopic properties of the prepared glass systems were investigated using X-Ray diffraction, Ultra-Violet (UV) spectroscopy, *Differential Scanning Calorimetry (DSC)*, Electron Paramagnetic Resonance (EPR – X band), Fourier Transform Infra Red (FTIR) spectroscopy and Raman spectroscopy. Present investigation is useful to study the effect of glass composition on the optical, thermal, physical properties and symmetry of the prepared glasses. Various physical properties for all the glasses were measured. X-ray diffraction of glass samples was carried to check its amorphous nature. From EPR spectra, the spin-Hamiltonian parameters were calculated and these parameters were influenced by the change in glass composition for different transition metal ions. The FTIR spectral investigations of glasses revealed characteristic vibrations of PO_4^{3-} units. The Raman spectra of all glass samples have displayed different spectral bands, and intensity of these bands. The results showed that the network structure of these glass samples is found to be change from glass to glass.

KEYWORDS:: Phosphate Glasses, *Differential scanning calorimetry*, UV-Vis; EPR, FTIR, Raman spectral studies.

I. INTRODUCTION

Modern technological applications have focused more attention in the studies of different types of glasses. Amongst wide variety glass systems, particularly, phosphate glasses are very important materials, because of their high thermal expansion coefficients, low optical dispersions and low glass transition temperature [1-3]. Phosphate glasses become particularly attractive in the field of optical technology in view of the fact that the fundamental optical absorption edge shift that would be caused by the introduction of metal oxide is the least in the case of phosphate glasses [4].

The phosphate based glasses containing transition metal ions are of huge interest because of their superior properties, which arise from the presence of transition metal ions in multivalent states [5,6]. Phosphate glasses doped with transition metal ions find a place in the new lasers and luminescence materials [7]. Chemical durability of phosphate glasses greatly improved by addition of ZnO because Zn ion acts as an ionic cross linker between different phosphate anions, inhibiting hydration reaction. In the present study, the authors report the optical, thermal and site symmetry studies of transition metal ions in calcium lead zinc phosphate glasses. Incorporation of $\text{V}_2\text{O}_5, \text{Cr}_2\text{O}_3, \text{MnO}$ and CuO is also expected to improve the chemical durability of the phosphate glasses. Therefore, it is interesting to study the effect of transition metal ions in calcium lead zinc phosphate glasses.

II. EXPERIMENTAL

2.1. Materials

Glasses with compositions, $20\text{CaO-}10\text{ZnO-}59.9\text{P}_2\text{O}_5\text{-}10\text{Pb}_3\text{O}_4\text{-}0.1x$, ($x= \text{V}_2\text{O}_5, \text{Cr}_2\text{O}_3, \text{MnO}$ and CuO) were prepared using analytical grade compounds of $\text{CaO}, \text{P}_2\text{O}_5, \text{Pb}_3\text{O}_4, \text{ZnO}, 0.1 \text{ mol\%}$ of $\text{V}_2\text{O}_5, \text{Cr}_2\text{O}_3, \text{MnO}$ and CuO . These chemicals were thoroughly mixed and ground for 30 min in a mortar pastel and then the charge was melted in a porcelain crucible using furnace for 5 h at temperature ranging from $800\text{-}1100^\circ\text{C}$ depending on composition. When the

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melt was thoroughly homogenized and attained desirable viscosity, it was poured onto brass plate. The prepared glass was annealed at appropriate temperatures (between 300 and 400 °C) for 2 h and stored in desiccators prior to evaluation. The formulae and process applied here to resolve the physical properties in the study were put to test in earlier works of the authors [8].

2.2. Experimental

XRD patterns for the glass powders were recorded in the 2θ range of $10-70^\circ$ on a computer controlled X-ray diffractometer (Model PW1170) with $Cu K_\alpha$ ($\lambda=1.5418 \text{ \AA}$) source. The differential scanning calorimetry (DSC) measurements were performed using Netzsch DSC 204 instrument. About 5-10 mg of the material was taken in an aluminum pan of the DSC setup and scanned at a heating rate of $10^\circ\text{C}/\text{min}$. The UV and visible optical transmissions for glass samples were measured by using JASCO model V-670 UV-Vis-NIR spectrophotometer covering the range 200-900 nm. EPR spectra were recorded at room temperature through BRUKER-ER073 series in the X-band frequency (9.4 GHz) at 100 kHz field modulation. The magnetic field was scanned from 0 to 800 mT and the microwave power used was 1mW. The IR infrared absorption spectra of the glasses were recorded at room temperature in the wave number range $4000-400 \text{ cm}^{-1}$ by SHIMADZU 8201 PC FT-IR spectrophotometer. The glass samples were subjected to Raman spectra in the range $200-3500 \text{ cm}^{-1}$ with Lab RAM HR-800-HORIBAJOBINYVON Raman spectrometer..

III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of calcium lead zinc phosphate glass system compositions. This figure shows a broad diffuse scattering at different angles instead of crystalline peaks (absence of Bragg Peaks) and no continuous or discrete sharp peak, which reflect the characteristics of amorphous glass structure.

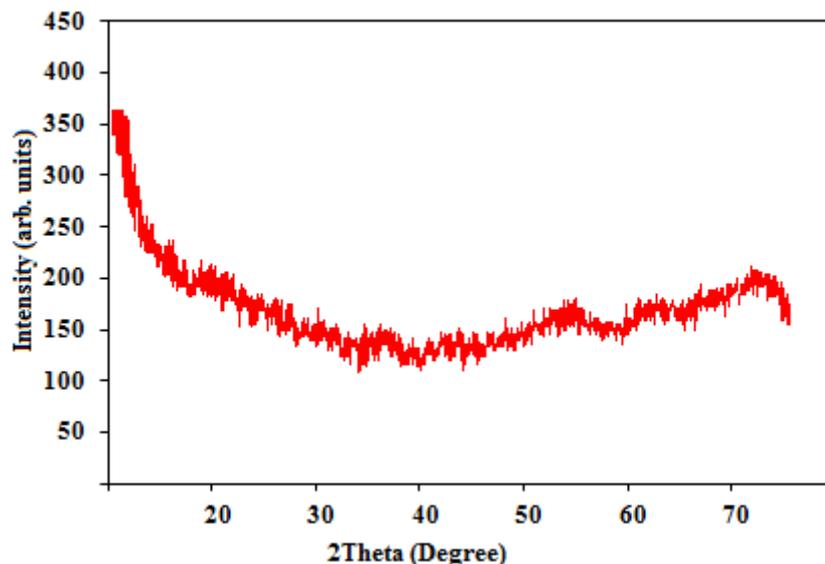


Fig. 1 XRD spectrum of $\text{CaO-Pb}_3\text{O}_4\text{-ZnO-P}_2\text{O}_5$ glass

Differential scanning calorimetry (DSC) is one of the most frequently used thermal analysis technique. DSC monitors heat effects allied with the phase transitions and chemical reactions as a role of temperature. DSC thermograms of present glass system are shown in Figure 2.

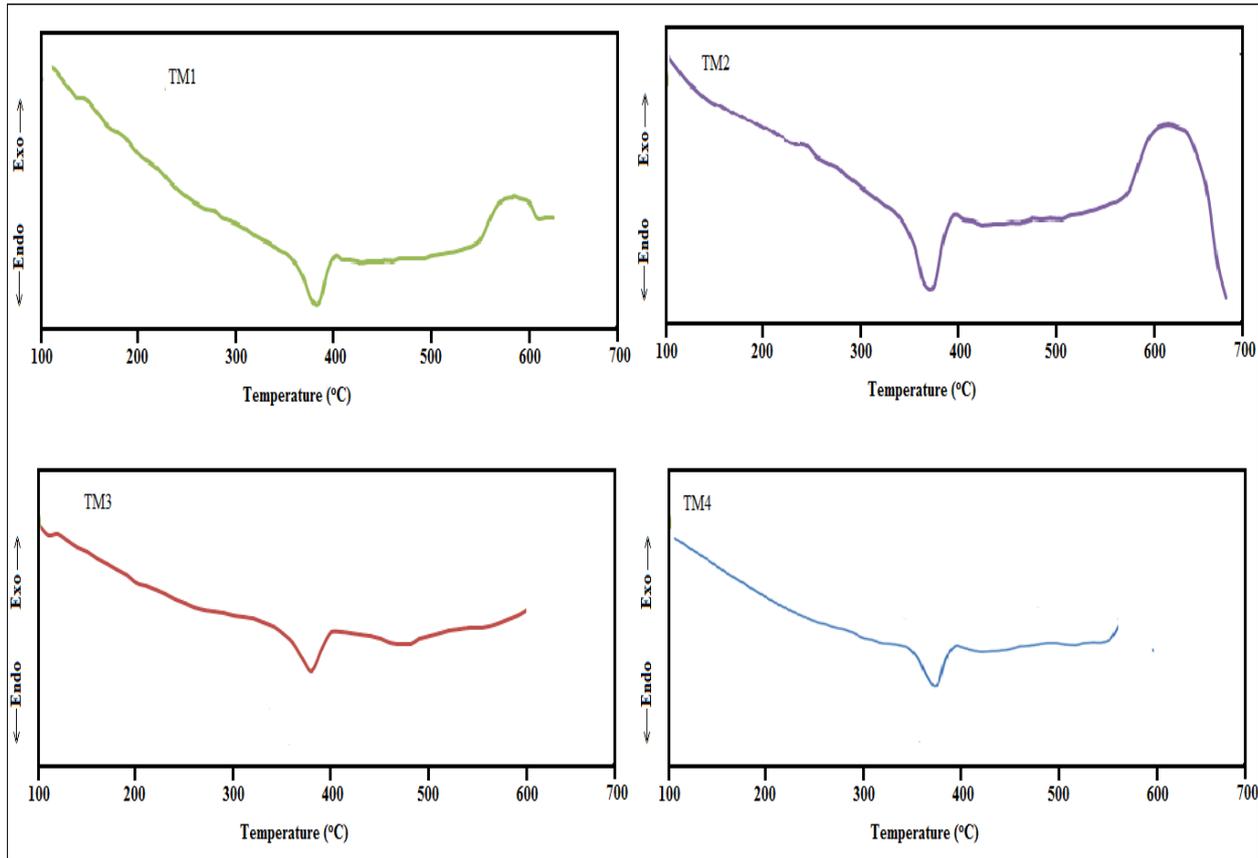


Fig. 2 DSC traces of transition metal ions doped CaO-Pb₃O₄-ZnO-P₂O₅ glass system

All the glasses exhibited an endothermic change due to the glass transition temperature (T_g) occurred between 350 °C and 370 °C. At higher temperatures, all the sampled glasses exhibited an exothermic change due to crystallization temperature (T_c) reported between 415 °C and 398 °C. The values of T_g , T_c and $T_c - T_g$ are presented in Table 1.

TABLE 1 Data on DSC traces of Transition metal ions doped CaO-Pb₃O₄-ZnO-P₂O₅ glasses

Sample	T_g (°C)	T_c (°C)	$T_c - T_g$ (°C)
TM1	353	402	49
TM2	370	415	45
TM3	365	406	41
TM4	362	398	46

The difference between crystallization temperature (T_c) and transition temperature (T_g) is an indication of thermal stability of glasses against crystallization. However, it may be noted that successive replacement of transition metal ions leads to a change in T_g . These observations clearly indicate a structural rearrangement of the phosphate glass network. The maximum value of $T_c - T_g$ is observed for TM1 glass, which indicates that TM1 glass is the most stable glass among TM2, TM3 and TM4.

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TABLE 2 Physical Properties of Transition metal ions doped CaO-Pb₃O₄-ZnO-P₂O₅ glasses

Physical property	TM1	TM2	TM3	TM4
Average molecular weight M (gm)	173.118	173.008	173.007	173.016
Density d (gm/cm ³)	3.6594	3.7121	3.6309	3.7876
Refractive indes (nd) at 589.3nm	1.6335	1.6210	1.6450	1.6200
Optical Dielectric constant (P∂t/∂p)	1.6683	1.6276	1.7060	1.6244
Dielectric constant (ε)	2.6683	2.6276	2.7060	2.6244
Reflection losses R(%)	5.7866	5.6136	5.9465	5.5999
Polaron Radius rp (A ⁰)	3.7176	3.7196	3.7135	3.6945
Interionic distance(A ⁰)	9.2221	9.1838	9.2172	9.2697
Molecular Electron Polarizabilty α(×10 ⁻²³ Cm ³)	6.7045	6.5037	6.8501	6.3632
Optical basicity Λ _{th}	0.4436	0.4439	0.4441	0.4442

From Table 2, it can be seen that change in the average molecular weight M, density significantly influences the physical properties such as dielectric constant, reflection losses, polaron radius, inter-ionic distance and electronic polarizability. From the data presented in Table 2, it can also be seen that, the physical properties are changing from glass to glass and hence the environment around the transition metal ions in these glasses also changes from glass to glass. The ideal values of optical basicity can be predicted from composition of glass and basicity moderating parameters of various cations present [9]. Basicity parameter slightly increases from glass TM1 to TM4. High optical basicity means high electron donor ability of oxide ions to the cations. Understanding of optical basicity is useful for the design of the novel optical functional materials like polarizer's, detectors and modulators with higher optical performances [10]. However, during the formation of glasses the orientation, arrangement and distribution of transition metal ions may differ in different glasses, which lead to different structural arrangements and bonding.

The absorption spectra of vanadium containing glasses are of very complex nature because of presence of three valance states of vanadium. In the present study of glasses, V₂O₅ doped glass attained the faint green colour and exhibited absorption bands at about 685 and 829 nm, as shown in Fig. 3(a). These absorption bands correspond to ²B_{2g} → ²B_{1g}, ²B_{2g} → ²E_g transitions, a characteristic of VO²⁺ ions [11]. The assignment of these bands has been made on the basis of an energy level scheme for molecular orbitals of VO²⁺ ion in a ligand field of C_{4v} symmetry [12]. VO²⁺ has never exhibited an ideal octahedral symmetry, but lowers to tetragonal (C_{4v}) [13]. Cr₂O₃ doped glass attained light green colour and the absorption bands appeared in the visible region nearly at 460, 630,660 and 690 nm, as shown in Fig.

3(b). Using Tanabe-Sugano diagrams for d^3 ions, the observed optical absorption bands are assigned to ${}^4A_{2g}(F) \rightarrow {}^2T_{1g}(F)$, ${}^4A_{2g}(F) \rightarrow {}^2T_{1g}(G)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^2E_g(G)$. The observed bands indicated that Cr^{3+} ions are present mostly in distorted octahedral coordination [14]. The presence of octahedral site is assumed to be related to the strong field stabilization energy of Cr^{3+} ions in sixfold coordination [15]. The UV- Visible absorption spectra of MnO doped lead zinc phosphate glass is shown in Fig. 3(c). The observed bands nearly at around 370, 406, 448 and 532 are assigned to the transitions ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$, ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)+{}^4E_g(G)$ and ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$, characteristic of Mn^{2+} ions in octahedral symmetry [16,17]. This analysis shows that manganese ions exist mainly in Mn^{2+} state, and occupy tetrahedral positions. The optical absorption spectrum is influenced by the host structure into which the transition metal ions are incorporated. In oxide glasses, the transition metal ions, mostly, form coordination complexes with doubly charged oxygen as the ligands. The optical absorption spectra for CuO doped glass is shown in Fig. 3(d). The optical absorption spectrum of the glass containing Cu^{2+} ions shows in a broad absorption band at about 825 nm, which can be attributed to the presence of Cu^{2+} ion and the octahedron being tetragonally distorted [18]. This absorption can be assigned to the ${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$ transition of Cu^{2+} ion.

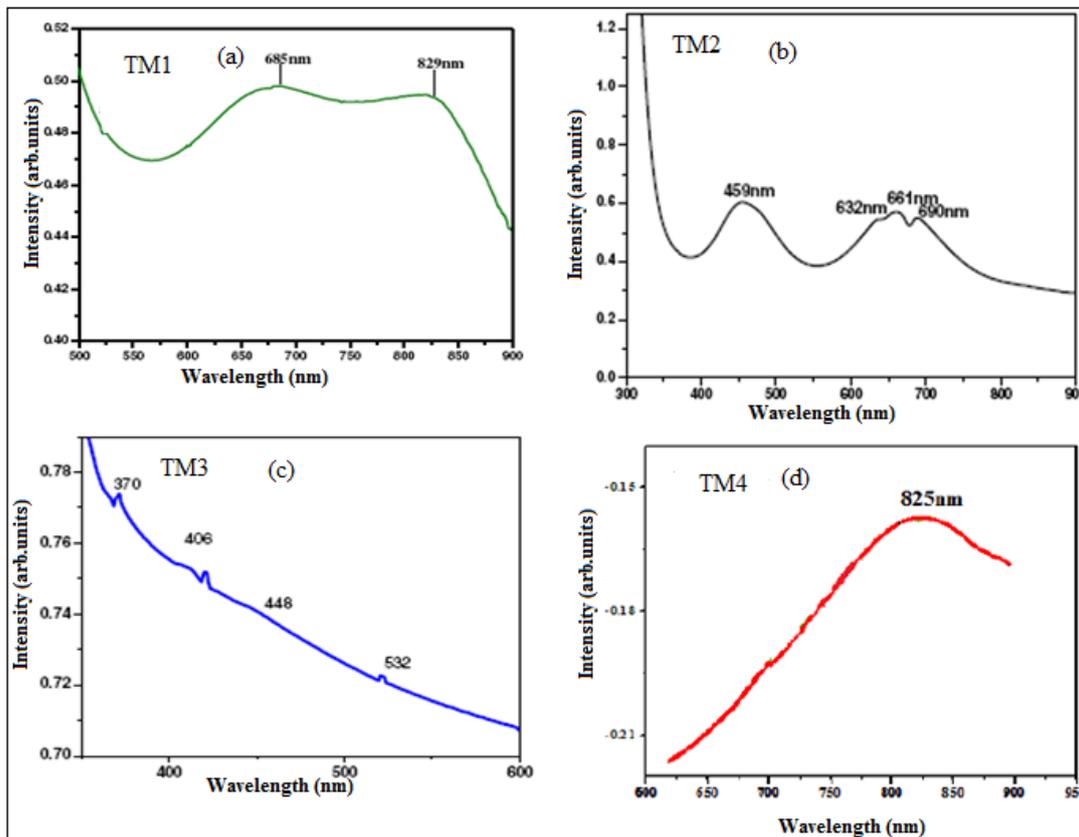


Fig. 3 Optical absorption spectra of transition metal ions doped CaO-Pb₃O₄-ZnO-P₂O₅ glass system

The cubic symmetry of Cu^{2+} ions is disturbed by electronic hole in the degenerate orbital which has caused the tetragonal distortion. However, Cu^{2+} , being as d^9 ion, experiences a strong Jahn-Teller distortion, which leads to the splitting of energy levels [18,20] and causes predominantly an elongated octahedral coordination with four short in-plane bond lengths and longer axial bond lengths. Table 3 shows the observed optical absorption band positions and the transitions of prepared glass samples. When all these absorption bands are correlated, the maximum absorption band observed is in case of Cu^{2+} doped glass while the remaining glasses contain more number of absorption bands.

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TABLE 3 Optical absorption band positions and transitions of Transition metal ions doped CaO-Pb₃O₄-ZnO-P₂O₅ glasses

Sample	Transitions	Wavelength (nm)	Wave number (cm ⁻¹)
TM-1	² B _{2g} → ² E _g	829	12062
	² B _{2g} → ² B _{1g}	685	14577
	² B _{2g} → ² A _{1g}	520	19193
TM-2	⁴ A _{2g} (F) → ² E _g (G)	690	14492
	⁴ A _{2g} (F) → ⁴ T _{2g} (F) (v ₁)	660	15151
	⁴ A _{2g} (F) → ² T _{1g} (G)	630	15873
	⁴ A _{2g} (F) → ⁴ T _{1g} (F) (v ₂)	460	21739
TM-3	⁶ A _{1g} (S) → ⁴ T _{1g} (G)	532	18796
	⁶ A _{1g} (S) → ⁴ T _{2g} (G)	446	22321
	⁶ A _{1g} (S) → ⁴ A _{1g} (G) + ⁴ E _g (G)	406	24630
	⁶ A _{1g} (S) → ⁴ T _{2g} (D)	370	27027
TM-4	² E _g (D) → ² T _{2g} (D)	825	12121

The EPR spectrum of V₂O₅ doped glass is shown in Fig. 4(a). Spectrum is observed to be complex made up of resolved hyperfine components arising from unpaired 3d¹ electron of ⁵¹V isotope. From the spectra, the values of g_{||}, g_⊥, A_{||} and A_⊥ are 1.952, 1.978, 176.477 and 60.23 respectively [21,22]. It is observed that g_⊥ > g_{||}, A_⊥ < A_{||}, confirmed that V⁴⁺ in the present glass exist as VO²⁺ ions in octahedral coordination with tetragonal compression. The symmetry of vanadyl complex is C_{4v}, and the ground state of 3d¹ ion is d_{xy}. EPR spectra of the Cr₂O₃ doped glass is shown in Fig. 4(b). The spectra exhibit two resonance signals at g = 1.9772 and g = 4.5617. Low field portion of spectrum is assigned to isolated Cr³⁺ ions and high field portion mainly due to exchange coupled Cr³⁺ ion pairs and is related to strongly distorted sites⁽²²⁾. The Resonance signal in high field region with 1.9772 is due to exchange of Cr³⁺ - Cr³⁺ pairs [23]. EPR spectra observed in MnO doped glass consist of a well resolved sextet centered at g = 2.0 with a broad background signal underside the sextet and well absorption centered at g = 4.3, which is characteristic of isolated Mn²⁺ ions in rhombic distorted octahedral environment, as shown in Fig. 4(c). It was concluded that resonance signal at g ≈ 2.0 is due to Mn²⁺ ion in an environment close to the octahedral symmetry [24]. The EPR spectrum of CuO doped glass is shown in Fig. 4(d). From the spectrum it is observed that g_e < g_⊥ < g_{||}, this order suggested that Cu²⁺ ion is situated in tetragonally distorted octahedral sites. spin-Hamiltonian parameters of the investigated samples were given in Table 4. By correlating all the EPR results, it is concluded that the spin-Hamiltonian parameters are influenced by the change in the glass composition with different transition metal ions.

TABLE 4 spin-Hamiltonian parameters of Transition metal ions doped CaO-Pb₃O₄-ZnO- P₂O₅ glasses

Spin Hamiltonian parameter	TM1	TM2	TM3	TM4
g-values	1.952 (g) 1.978 (g _⊥)	4.561 1.977	4.3 2.0	2.464 (g) 2.095 (g _⊥)
A-values	176.477(A) 60.230(A _⊥)			100.5(A) 25.2(A _⊥)
Δg	0.974			1.230
Δg _⊥	0.987			1.046

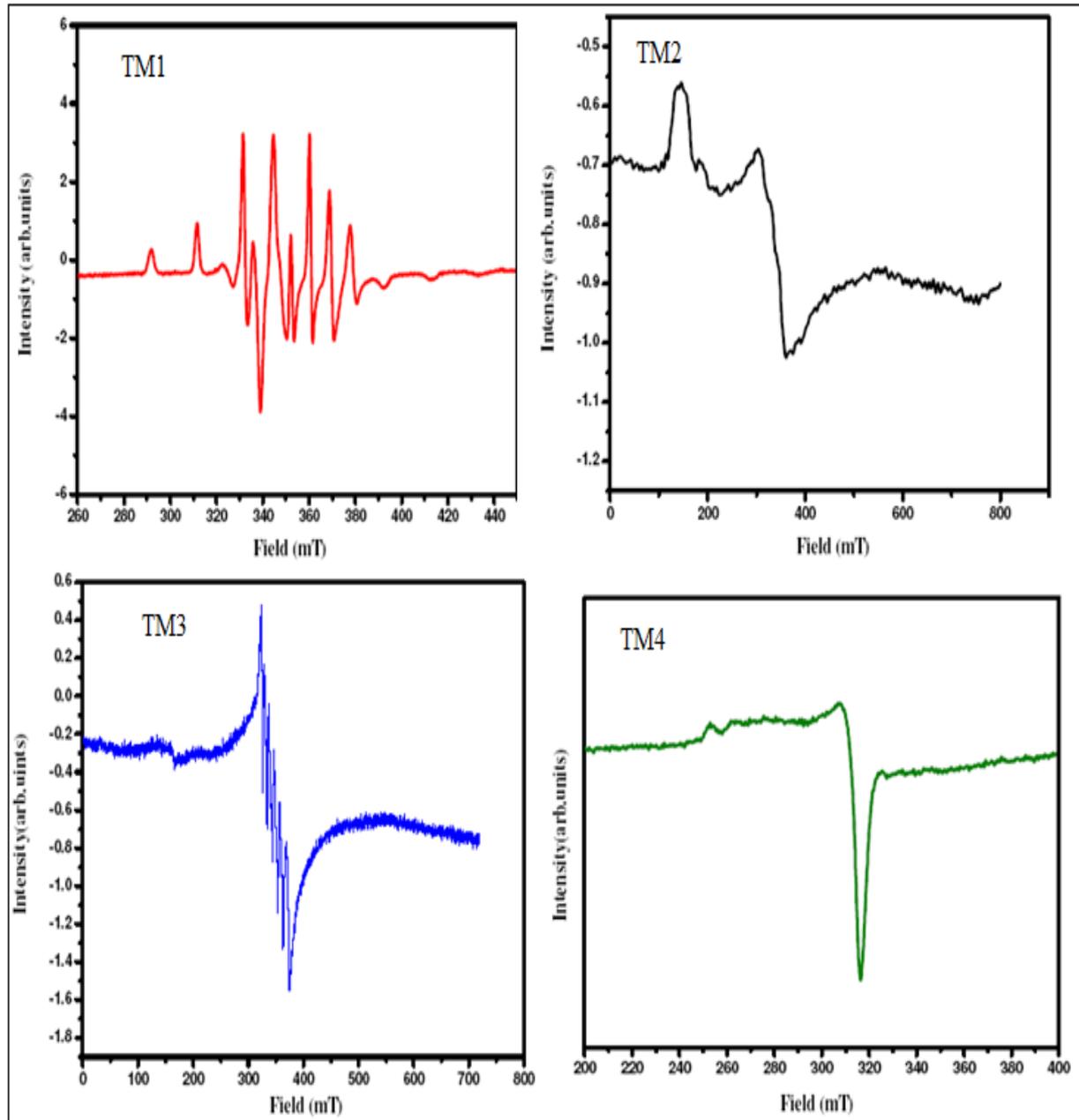


Fig. 4 EPR spectra of transition metal ions doped CaO-Pb₃O₄-ZnO-P₂O₅ glass system

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Figure 5 shows the infrared spectra of the present glass samples. The FTIR spectra exhibited several peaks, which can be divided as medium and broad. Similar to other phosphate glasses, the present samples also exhibited the main characteristic active vibrational modes of phosphate network in the range $1400 - 600 \text{ cm}^{-1}$. The bands at 1180 cm^{-1} are assigned to the vibrations of PO_3^{2-} groups at the end of chains [25]. The bands observed at $< 600 \text{ cm}^{-1}$ are related to phosphate network bending vibrations [26]. The bands at $\sim 1080 \text{ cm}^{-1}$ are due to PO_4^{3-} fundamental vibrational modes. Band at 1020 cm^{-1} is due to the symmetric stretching vibrations of the (PO_4^{3-}) tetrahedra (P-O- ionic group) [27]. The fundamental band at 980 cm^{-1} is observed in case of all samples and it is an indication of phosphate ions in *p* state, exist in tetrahedral symmetry and the bands in 950 cm^{-1} region are due to the asymmetric stretching vibrations of P-O-P groups [28]. Bands at 720 and 730 cm^{-1} are due to symmetric vibration the P-O-P chains. FTIR spectroscopy establishes the type of structural units, whose number increases with the successive replacement of the TM content.

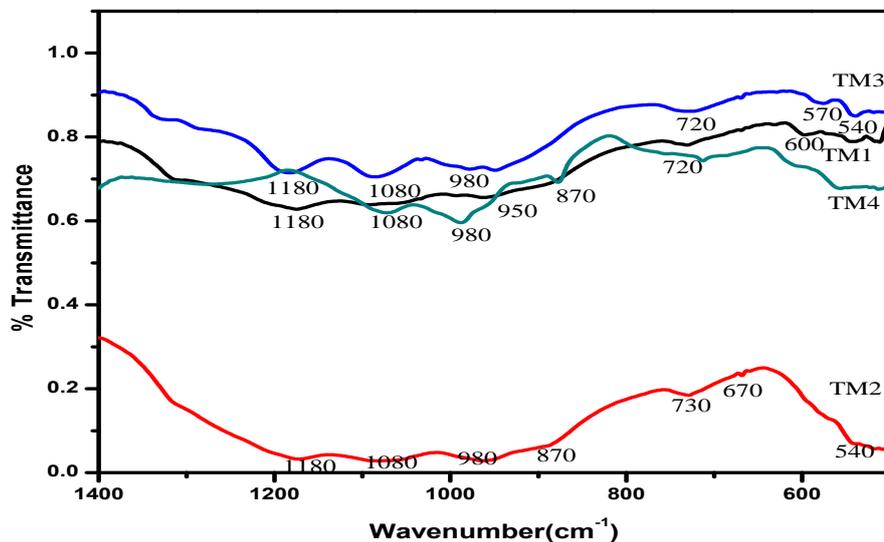


Fig. 5 FTIR spectra of transition metal ions doped $\text{CaO-Pb}_3\text{O}_4\text{-ZnO-P}_2\text{O}_5$ glass system

The most important bands observed in Raman spectra (Fig. 6) are $330\text{-}340 \text{ cm}^{-1}$ assigned to the bending vibration of the phosphate polyhedral [29], the band at 670 cm^{-1} is reported to be symmetric stretch mode of the bridging oxygen atoms on Q^2 tetrahedra (P-O-P) [30]. P-O-P asymmetric stretching vibration mode is assigned to 750 cm^{-1} band position, a shoulder at $\sim 910 \text{ cm}^{-1}$ and a band at $\sim 1020 \text{ cm}^{-1}$ which is appropriate to assign to the P-O stretching modes [29,31]. The band at $\sim 1100 \text{ cm}^{-1}$ is due to $(\nu_s(\text{PO}_2^-))$ mode [32], the bands at 1140 cm^{-1} and 1170 cm^{-1} are attributed to (P-O) stretch and $(\text{PO}_2)_{\text{sym}}$ stretch, Q^2 units [33]. The characteristic bands of PbO appear at low frequencies ($330\text{-}340 \text{ cm}^{-1}$). The bands are specific for lead and seem to be independent of the oxygenated glass former and these bands are characteristic of yellow β - PbO and this may indicate that the lead, in these samples, is involved in some structural arrangements [34]. Therefore, Raman spectra conclude that the studied glasses consist of specific bands for the phosphate groups and addition of TM oxides (V_2O_5 , Cr_2O_3 , MnO and CuO) leads to change in glass network.

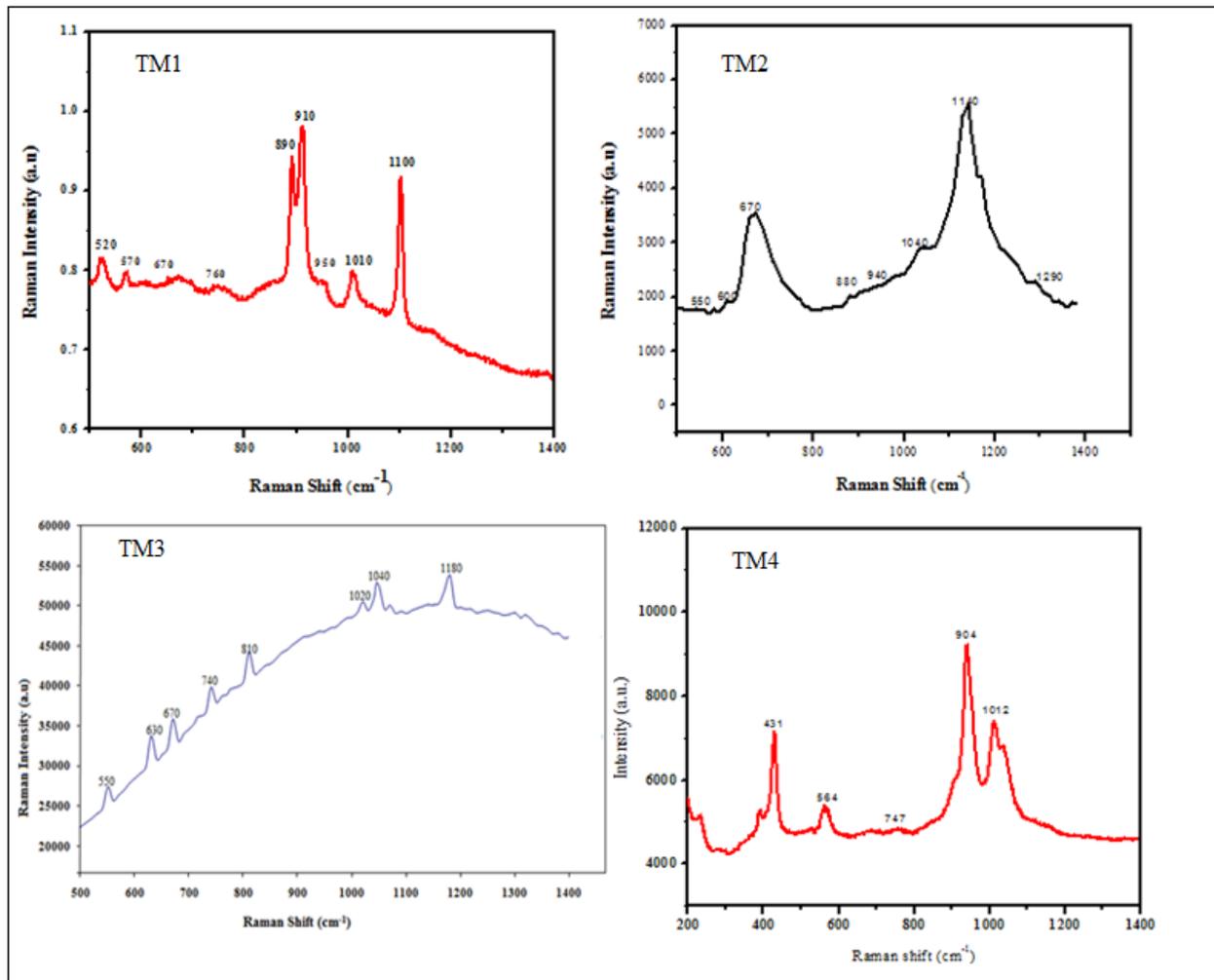


Fig. 6 Raman spectra of transition metal ions doped CaO-Pb₃O₄-ZnO-P₂O₅ glass system

IV. CONCLUSIONS

The structures of studied glasses can be considered as phosphate units connected with VO²⁺, Cr³⁺, Mn²⁺ and Cu²⁺ ions in tetragonally distorted octahedral sites. DSC results indicate that vanadium ions increase cross-link density and enhance mean bond strength in TM1 glass. From the optical absorption spectra, the broad and a sharp absorption band observed in Cu²⁺ doped glass while the remaining glasses contain more number of absorption bands. EPR results conclude that the spin-Hamiltonian parameters are influenced by the change in the glass composition with different transition metal ions. FTIR and Raman spectra exhibited the main characteristic active vibrational modes of phosphate network and successive replacement of transition metal oxides leads to change in site symmetry of the prepared glasses.

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