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Influence of Mo^{5+} ions on spectroscopic properties of $PbO-ZnF_2-P_2O_5$ glass system

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Abstract

Physical and spectral properties like density, optical absorption, infrared and ESR spectral studies are measured for lead fluorophosphate glasses doped with molybdenum ions. The melt quenching technique was used for the preparation of standard samples of $PbO-ZnF_2-P_2O_5$ glass system in the compositional series containing 0.1, 0.2, 0.3, 0.4, 0.8 and 1.0 mol% of molybdenum. Spectroscopic studies, ESR, optical absorption and IR reveal the presence of molybdenum ions with the MoO_4 and MoO_6 structural groups in these glasses. The oxidation state of molybdenum are mostly existing in Mo^{5+} up to 0.2 mol% beyond that concentration exist in Mo^{6+} state.

Keywords: $PbO-ZnF_2-P_2O_5$ glasses; Optical absorption; IR and ESR spectroscopic studies

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1. Introduction

Distinctive properties are the advantages to the phosphate glasses for the extensive applications. The modest chemical durability [1] restricts the usefulness of the phosphate glasses but, the addition of several oxides like PbO [2] improves the chemical durability of these glasses. At the point when PbO enters the system, it is relied upon to shape PbO_4 units in which lead is facilitated to four oxygens in a covalently bonded configuration [3,4]. A few properties of phosphate glasses have been found to come about because of PbO into the system: for occurrence PbO is helpful for protecting against high energy radiations, including atomic radiation [5,6]. The improved chemical durability Lead phosphate glasses [7,8] possesses high coefficients of thermal expansion and also expose good optical properties. In $PbO-P_2O_5$ glasses it was found that [9] Pb^{2+} ions possess a position between P−O−P layers. Fluoride glasses commonly have infrared absorption edge wavelengths in the range between 6 and 8 μm. Phosphate glasses broaden their transmitting range into the infrared [10] with the incorporation of ZnF_2.

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Transition metal oxide ions of oxide glasses are of greater importance, since these ions exist in multivalent oxidation states in a glassy matrix exhibiting interesting behaviors like electronic, optical, and magnetic properties [11−13]. Among diverse sorts of glass formers, the phosphate glasses are considered to be significant in nature because of their possessing good thermal expansion coefficient, lower refractive index, with an extended transmission ability from near UV to middle IR demonstrating their suitability as luminescent potential optical materials [14−16]. Phosphate glasses of transition metal oxides are of persistent attention, since these glasses have potential applications in devices like optical switching, electrical threshold and memory switching [17]. Physical properties and the chemical durability of phosphate glasses can be enlightened by adding various glass formers and modifiers, for example, MoO_3, TiO_2, Al_2O_3, Ta_2O_3, As_2O_3 and so on, into P_2O_5 glass system [18,19].

A remarkable two-dimensional layered structure [20] of MoO_3, one of the oxide semiconductors in orthorhombic state have unlimited potentials in the gas sensors, memory devices and optical smart windows [21]. Glasses containing MoO_3 have been the subject of many.

investigations due to their catalytic properties. Mo−O bond in molybdenum hexavalent oxide is identified as significantly covalent. Depending on the concentration and nature of the host network molybdenum ions act both network formers and network modifiers with the two steady valence states, Mo (V) and Mo (VI) in the glass system.

2. Experimental procedures

2.1. Glass sample synthesis

The samples used for the present study are prepared by analytical grade reagents, by using the melting and quenching techniques [22−24]. The sample compositions synthesized of the formula (10-X) PbO−20 ZnF_2−70 P_2O_5−X MoO_3 where X = 0, 0.1, 0.2, 0.3, 0.4, 0.8 and 1.0 mol%. The analytical grade chemicals PbO, ZnF_2, P_2O_5 and MoO_3 were mixed thoroughly using an agate mortar and melted in a platinum crucible at about 1200 K using PID temperature controlled furnace at about 1 h to get a bubble free liquid homogeneous melt. The resultant melt was quickly quenched by pouring into a brass mould and the glass samples were annealed at 500 K for 2 h. The prepared samples were optically polished as well as the surfaces are made perfectly smooth.

2.2. Physical properties

Density of all glass samples was determined at room temperature by standard principle of Archimedes' using O-xylene as the immersion liquid. Average molecular weight $\overline{M}$, ion concentration N_i, inter ionic distance r_i and polaron radius r_p have been calculated and shown in Table 1.

2.3. X-ray diffraction

X-ray diffraction confirms the amorphous nature of the prepared glass samples. SEIFERT diffractometer model SO-DEBYE FLUX 202 was used for the characterization of X-ray diffraction analysis of the prepared samples.

2.4. Spectroscopic properties

The optical absorption spectra of the glass samples were recorded at room temperature using a JASCO UV-VIS-NIR Spectrophotometer in the wavelength range 350−950 nm. The principle of microwave spectrometer used for Electron Spin Resonance (ESR) spectra of $PbO-ZnF_2-P_2O_5$ glasses doped with MoO_3 were recorded using E11Z Varian X-band (ν = 9.5 GHz) ESR spectrometer. Infrared transmission (IR) spectra of the samples were recorded using a Bruker IFS 66 V − IR spectrophotometer in the wavenumber range 400−1600 cm^{-1} by potassium bromide (KBr) pellet method.

Table 1
Data on various physical properties of $PbO-ZnF_2-P_2O_5$: MoO_3 glasses.

Glass	Density (g/cm^3) (±0.0001)	Average molecular weight ($\overline{M}$)	Conc.of molybdenum ions N_i (x 10^{21} ions/cm^3)	Inter ionic distance r_i (A°)	Polaron radius r_p (A°)
M_0	2.7018	116.5	–	–	–
M_2	2.7099	116.7	2.79	7.09	2.86
M_3	2.7105	116.7	4.19	6.20	2.50
M_4	2.7176	116.8	5.66	5.63	2.27
M_8	2.7870	117.2	11.458	4.44	1.79
M_{10}	2.8210	117.4	12.356	4.33	1.74

3. Results

Fig. 1 shows the X-ray diffraction pattern of the prepared glasses and indicates no line of diffraction that confirms the amorphous nature of the glass samples.

The optical absorption spectra of $PbO-ZnF_2-P_2O_5$ glass containing MoO_3, recorded at room temperature in the wavelength region 350−950 nm (Fig. 2). The absorption edge observed at 396 nm for pure glass M_0 is observed to shift towards slightly higher wavelength side with increase in the concentration of MoO_3 up to 0.2 mol% and beyond 0.2 mol% the absorption edge shifted towards slightly lower wavelength. The spectra of the glasses exhibited a broad absorption band in the region 600−800 nm corresponding to $^2B_2 \rightarrow ^2B_1$ [25−27] transition of Mo^{5+} ions. The half width and peak height of absorption bands are observed to increase, with increase in the concentration of MoO_3 up to 0.2 mol%. We have evaluated the optical band gaps (E_o) of these glasses by drawing the Urbach plots (Fig. 3) and inset shows the variation of optical band gap with the concentration of MoO_3. The values of optical band gap (E_o) obtained from the extrapolation of these curves are presented in Table 2; the value of E_o is found to be the minimum for glass M_2.

The infrared transmission spectra of $PbO-ZnF_2-P_2O_5$: MoO_3 glasses (Fig. 4) shows all the spectra represents characteristic peak corresponding to different vibration modes of PO_4 tetra as well as P−O−P bonds. The spectrum of molybdenum free glass (M_0) showed vibrational bands at 1345 cm^{-1} (because of P=O stretching vibrations), 1286 cm^{-1} (identified due to antisymmetric vibrations of PO_2^- groups), 1091 cm^{-1} (band due to symmetric stretching normal vibrational mode in PO_4^{3-} units), 1008 cm^{-1} (due to PO_3 units and may also consisting a band due to P−O−P asymmetric stretching vibrations) and another band at 759 cm^{-1} due to P−O−P symmetric stretching vibrations and may also consist of bands due to pyrophosphate groups ($P_2O_7^{4-}$) [28−30]. The band at 470 cm^{-1} is due to the bending vibrations of P−O−P sharing with the Pb−O or Pb−O−P vibrations [31,32]. A band due to PbO_4 structural units is also identified at the same region.

The bands due to MoO_4 and MoO_6 structural units could also be located at 898 and 708 cm^{-1} respectively. With the increasing concentration of MoO_3 up to 0.2 mol%, an increase in the intensity of asymmetrical bands due to phosphate groups and also MoO_6 structural units could clearly be observed. Beyond 0.2 mol% increase of MoO_3, the symmetrical bands are detected to increase at the expense of asymmetric bands with a shift towards lower wave number; in this concentration range, the band due to MoO_4 structural units has also shown an increasing tendency. The band position of different structural groups of phosphate and molybdate mentioned in the present glasses are observed to be within the ranges specified in the literature [33,34] and the intensity variation of the

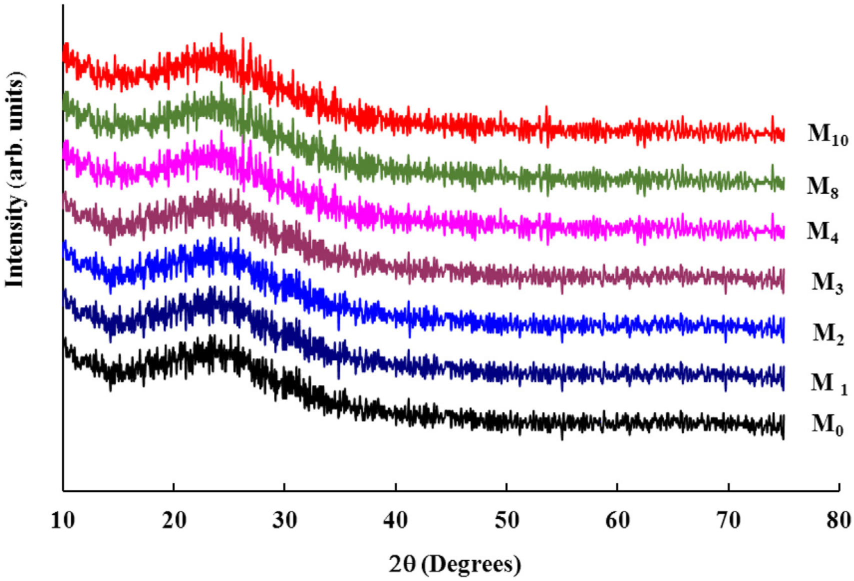

Fig. 1. XRD pattern of $PbO-ZnF_2-P_2O_5$: MoO_3.

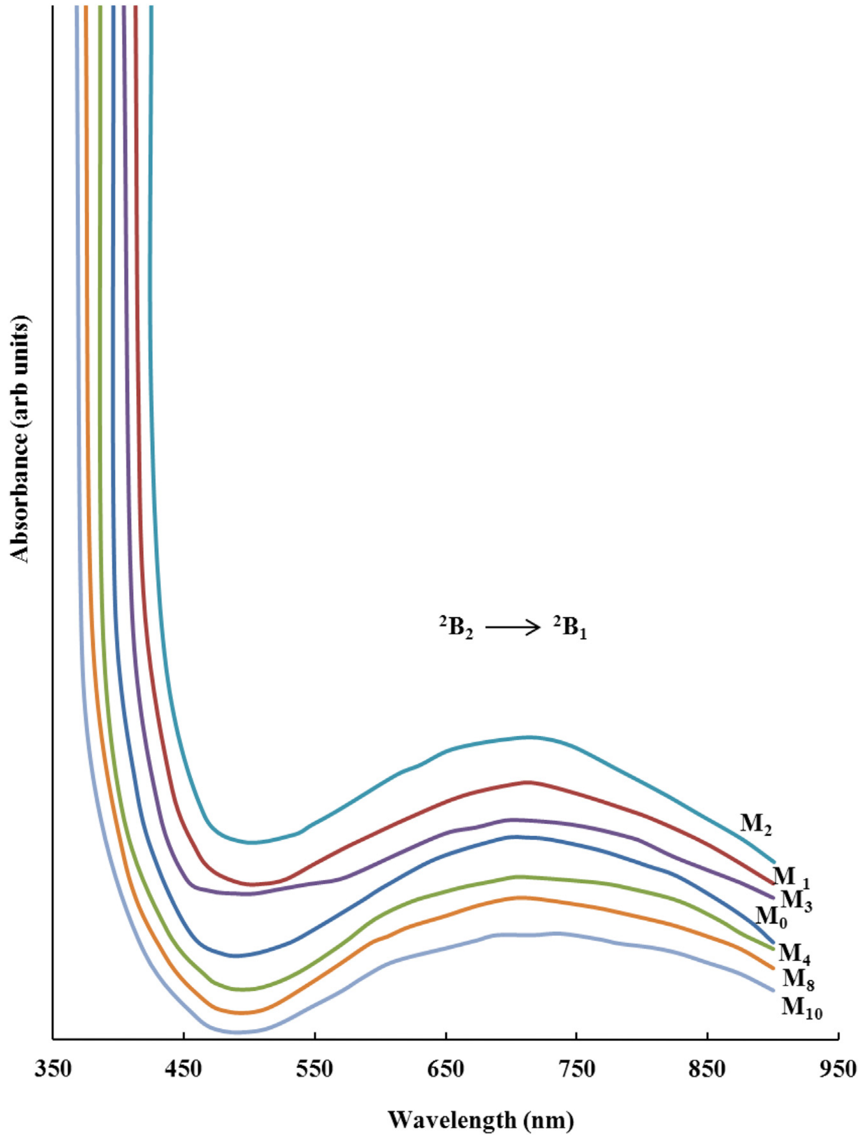

Fig. 2. Optical absorption spectra of $PbO–ZnF_2–P_2O_5$: MoO_3 glasses.

bands with the concentration of MoO_3 is presented in Fig. 5.

The values of g⊥ and gll have been calculated from the ESR spectra and tabulated in Table 3. ESR spectra of $PbO–ZnF_2–P_2O_5$ containing MoO_3 glasses recorded at room temperature exhibited a central line at g⊥ = 1.932 and gll = 1.872 (Fig. 6) and the variation of intensity with the concentration shown in inset figure. With the increase in the concentration of MoO_3 both intensity and half width ($\Delta B_{1/2}$) of the central line are found to increase up to 0.2 mol% and there after a slight decrease in the half–width is noticed.

4. Discussion

A well-known strong glass forming oxide, phosphorous pentoxide participates in the glass network with PO_4 structural units. One of the four oxygen atoms in PO_4 tetrahedron is doubly bonded to the phosphorus atom with the substantial π-bond character to account for pentavalency of phosphorous [35]. In general, the P–O–P bond between PO_4 tetrahedra is much stronger than the cross bond between chains via the metal cations [36]. When glass modifier PbO enters the glass network structure behaves like a defect in the

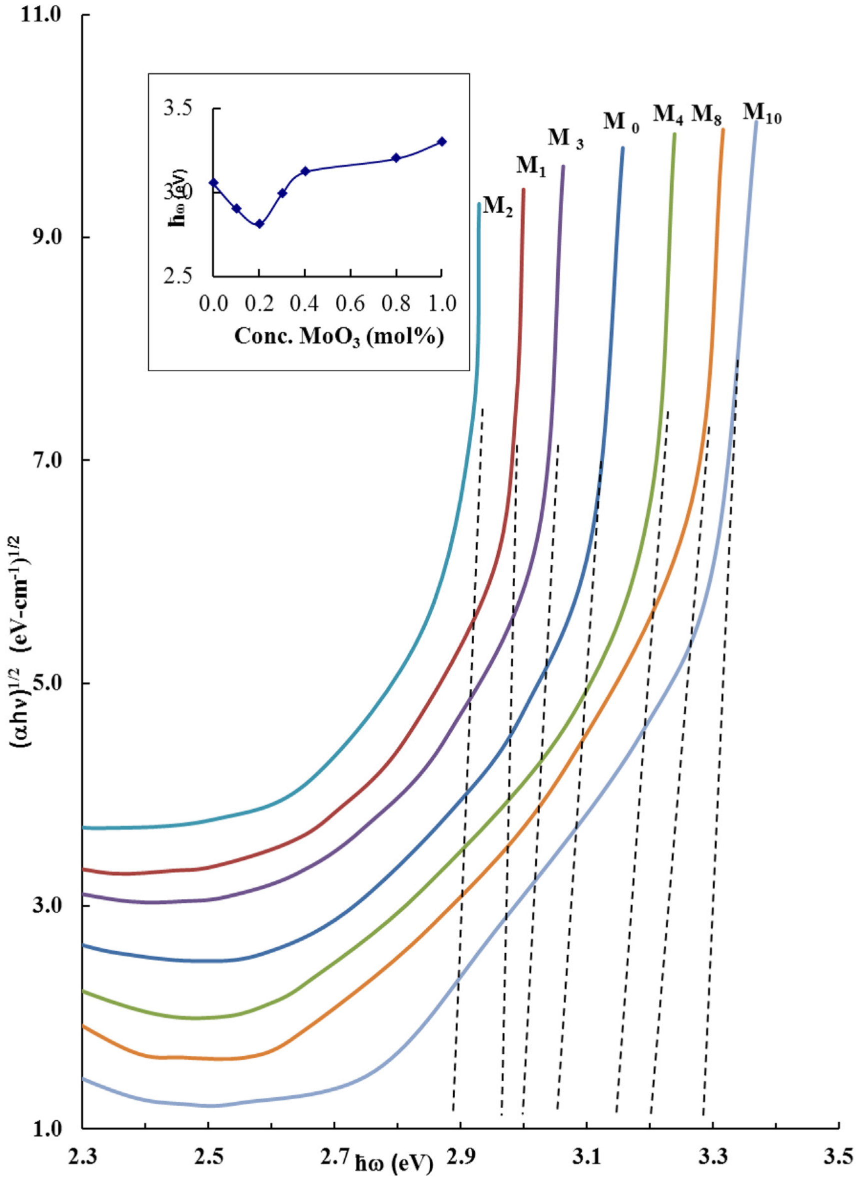

Fig. 3. Urbach plot of PbO–ZnF$_2$–P$_2$O$_5$: MoO$_3$ glasses. Inset (a) shows the variation of optical band gap with concentration of MoO$_3$.

Table 2
Data on optical absorption spectra of PbO–ZnF$_2$–P$_2$O$_5$: MoO$_3$ glasses.

Glass	Cut-off wavelength (nm)	Band position (nm)	Optical band gap (eV)
M$_0$	396	703	3.05
M$_1$	413	719	2.96
M$_2$	425	723	2.87
M$_3$	404	713	2.99
M$_4$	386	702	3.15
M$_8$	375	695	3.20
M$_{10}$	368	689	3.28

network of P_2O_5 [37]. In this case the lead ions are octahedrally positioned and the network structure is considered to build up from PbO_4 units [38] and alternate with PO_4 structural units and may form the Pb–O–P linkages shown in IR spectra.

The intermediate glass forming molybdenum oxide is an incipient glass network former, does not readily form the glass but does in the presence of the modifier oxide ZnF_2 with MoO_4^{2-} structural units and it may also act as modifier with MoO_6 and $Mo^{5+}O^{3-}$ structural groups. In the present glass system, molybdenum ions are expected to exist mainly in Mo^{6+} state. Our visual examination

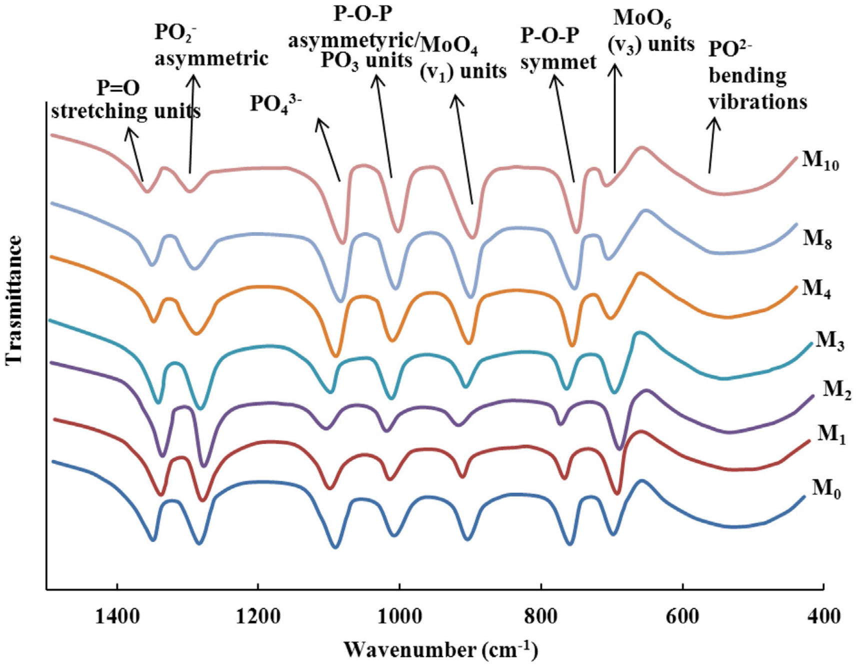

Fig. 4. IR Spectra of $PbO—ZnF_2—P_2O_5$: MoO_3 glasses.

showed as the concentration of MoO_3 is increased, the coloration of the samples turn into increasingly blue, indicating the reduction of a part of molybdenum ions from Mo^{6+} state to Mo^{5+} state [39]. Due to the Jahn-Teller effect, these Mo^{5+} ions are quite stable and occupy octahedral positions with distortions [40,41].

In IR spectra the intensity of bands due to PO_2^- groups and PO_4^{3-} groups are observed to grow at the expense of symmetric stretching P=O bonds and P—O—P rings. The band due to υ_1 vibrational mode of MoO_4^{2-} tetrahedral units located at about 898 cm^{-1} is observed to be shifted towards a region of higher wave number; in this region the band due to the strongly deformed MoO_6 groups is expected [42]. Similarly the υ_3 vibrational band of MoO_4^{2-} units is shifted towards on the region of asymmetric stretching vibrations [43].

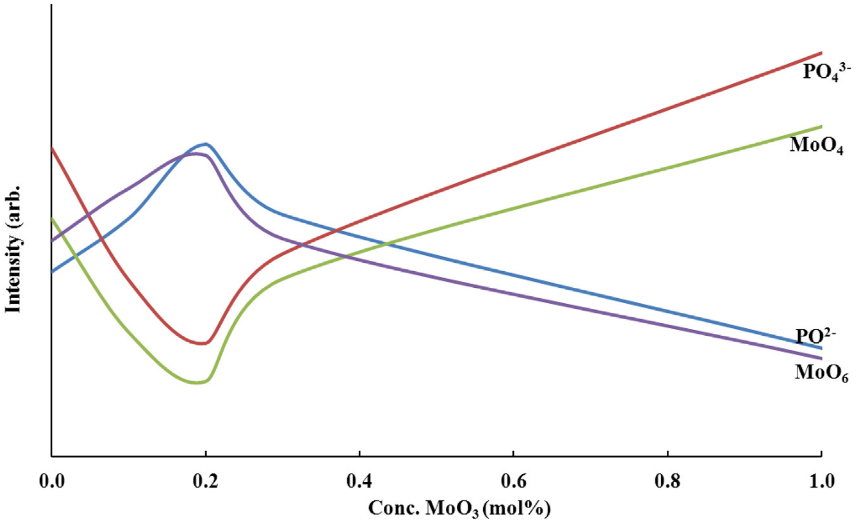

Fig. 5. Comparision plot of intensity of various structural units with the concentration of MoO_3 for $PbO—ZnF_2—P_2O_5$:MoO_3 glasses.

Table 3
Data on ESR spectra of PbO–ZnF_2–P_2O_5: MoO_3 glasses.

Glass	$g_\perp$	$g_{\|}$	$\Delta B_{1/2}$ (mT)
M_0	1.943	1.880	7.23
M_1	1.938	1.874	8.09
M_2	1.932	1.872	8.45
M_3	1.940	1.877	7.81
M_4	1.954	1.883	6.68
M_8	1.958	1.885	6.14
M_{10}	1.961	1.889	5.83

These results confirm transformation of molybdenum ions from tetrahedral positions to octahedral positions with increase in the concentration of MoO_3. Thus the results of IR spectral studies point out that there is a decreasing degree of disorder in the glass network when MoO_3 is present in higher concentrations (>0.2 mol%).

Broad absorption band observed in the region of 600–800 nm in the optical absorption spectra of these glasses is assigned to the excitation of Mo^{5+} (4 d^1) ion. In fact, for this ion, two optical excitations were anticipated starting from b_2 (dxy) ground state to (dxz-

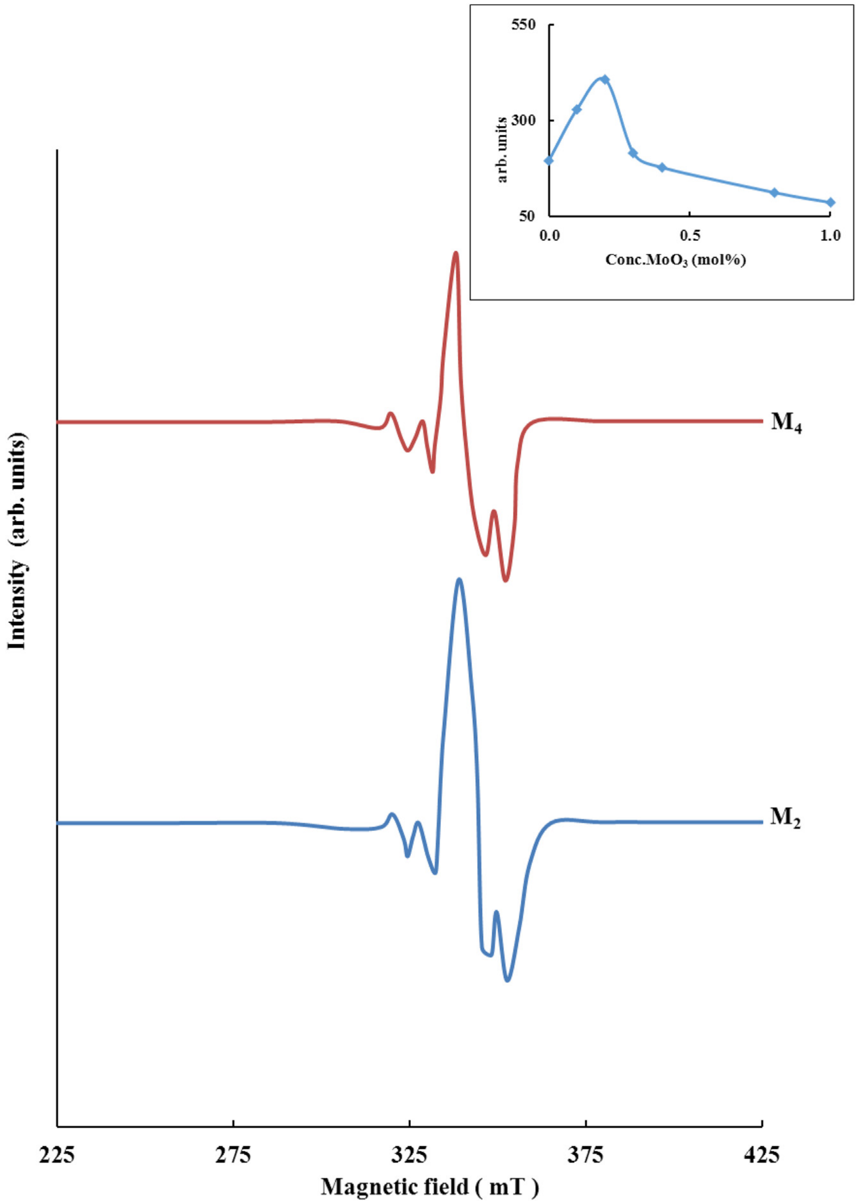

Fig. 6. ESR spectra of PbO–ZnF_2–P2O_5: MoO_3 glasses. Inset represents the variation of intensity with concentration.

yz) and (dx^2-y^2) with [44]. Maybe, due to inter charge transfer of Mo^{5+} and Mo^{6+} in the glass network, the resolution of these transitions could not be noticed. The highest intensity of this band observed in the spectrum of glass M_2 reveals the presence of Mo^{5+} ions in higher concentration in these glasses due to the depolymerization of the glass network [45] that create bonding defects and NBOs of Mo^{5+} ions. A substantial shrinkage in the band gap is developed due to overlap of localized electrons initially in Mo^{5+} sites with the neighboring Mo^{6+} sites with the increasing concentration of MoO_3. This may give the clarification of the reduction in the optical band gap with an increase in the concentration of molybdenum.

In the ESR spectra, the central line arises from even molybdenum isotopes (I = 0) and the.

smaller lines correspond to the hyper fine structure from odd ^{95}Mo and ^{97}Mo (I = 5/2) isotopes [46]. The signal at $g\perp = 1.943$ and $gll = 1.886$, detected in the ESR spectrum is obviously due to Mo^{5+} (4 d^1) ions. The variation of MoO_3 content has considerably affected the intensity of the signal, we have also observed the rise in the intensity and the half width $\Delta B_{1/2}$ of the signal with increase in the concentration of MoO_3 up to 0.2 mol% and for further increase of MoO_3, the signal is observed to be feeble. All these observations suggest that the molybdenum ions (Mo^{6+} ions) that participate in the glass network with MoO_4^{2-} structural units is higher in the samples (M_3 to M_{10}) and high intensity signal of the samples M_0 to M_2 indicates higher concentration of Mo^{5+} ions that act as modifiers in the glass network.

5. Conclusion

In conclusion, the analysis of the results of various spectroscopic studies, optical absorption and ESR spectral studies of $PbO-ZnF_2-P_2O_5$ glass containing MoO_3, indicates that there is a possibility of conversion of a part of Mo^{6+} ions into Mo^{5+} ions, especially when the concentration of MoO_3 is less than 0.2 mol%. These Mo^{5+} ions mostly act as modifiers and weaken the glass network. The IR spectral studies indicate that the molybdenum ions occupy octahedral positions when concentration of MoO_3 is beyond 0.2 mol% and the molybdenum ions occupy tetrahedral positions in larger concentrations in sample M_2 and increase the rigidity of the sample.

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