

Magnetic and spectroscopic studies on molybdenum ions in $\text{CaF}_2\text{-PbO-P}_2\text{O}_5$ glass system

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Abstract. $\text{CaF}_2\text{-PbO-P}_2\text{O}_5$ glasses containing different mole fractions of MoO_3 (ranging from 1.0 to 20 %) were prepared. Magnetic susceptibility, ESR and Optical absorption, spectral studies on these glasses have been carried out. Interesting changes observed in these properties with the variation in the mole fraction of MoO_3 have been discussed in the light of various oxidation states of molybdenum ions.

Keywords: Optical absorption; Magnetic Susceptibility; ESR

INTRODUCTION

P_2O_5 glasses have attracted extensive research interest in recent years due to their outstanding physical properties such as high thermal expansion coefficients, low melting and softening temperatures and high ultraviolet transmission.^{1–10} However, the poor chemical durability, high hygroscopic and volatile nature of phosphate glasses have prevented them from matching the performance of conventional glasses in a wide range of technical applications. In recent years, there has been an enormous amount of research on improving the physical properties and the chemical durability of phosphate glasses by introducing a number of heavy metal oxides into the P_2O_5 glass network.^{11–14}

The addition of PbO is expected to make these glasses more moisture resistant, since PbO , in contrast to the conventional alkali oxide modifiers, has the ability to form stable glasses due to its dual role – one as modifier (with PbO_6 structural units, if Pb-O is ionic) and the other as glass former (with PbO_4 structural units, if Pb-O is covalent). The covalent character of PbO in the glass network is attributed to the strong interaction of easily polarizable valence shells of Pb^{2+} ions with the highly polarizable O^{2-} ion.^{15,16} PbO mixed glasses may also be of particular interest for non-linear optical effects, when doped with rare earth ions. The IR harmonic and anharmonic electron-phonon modes are expected to contribute significantly to the non-linear optical susceptibilities in these glasses. Wasylak and Kityk have carried out extensive investigations of a variety of PbO mixed glass systems along these lines.^{17–19} Addition of CaF_2 further into lead phosphate

glass matrices is predicted to lower the viscosity and to decrease the liquidus temperature to a substantial extent and is also found to act as effective mineralizer.²⁰

MoO_3 containing glasses have been the subject of many investigations due to their catalytic properties. The ions of molybdenum inculcate high activity and selectivity in a series of oxidation reactions of practical importance in the glass matrices.^{21,22} A considerable number of interesting studies are available on the environment of molybdenum ion in various inorganic glasses.^{23–28} Mo-O bond in molybdenum hexavalent oxide is identified as significantly covalent. The Mo ion exists at least in two stable valence states viz., Mo^{V} and Mo^{VI} in the glass network. Molybdenum ions act both as network formers as well as network modifiers depending upon their concentration and nature of the host network. Most of the studies available on MoO_3 containing glasses are on the understanding of their structure by spectroscopic investigations^{29–31} and ionic conductivity studies.³²

The present investigation is aimed at an understanding of the local environment of molybdenum ions in $\text{CaF}_2\text{-PbO-P}_2\text{O}_5$ glass matrix and their influence on the stability of the glass network by means of the magnetic studies (magnetic susceptibility and ESR spectra) and optical absorption spectral data.

EXPERIMENTAL

Within the glass-forming region of $\text{CaF}_2\text{-PbO-P}_2\text{O}_5$ glass system the following composition is chosen for the present study.

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- M₀: 10 CaF₂-30 PbO-60 P₂O₅
 M₁: 10 CaF₂-30 PbO-59 P₂O₅: 1 MoO₃
 M₅: 10 CaF₂-30 PbO-55 P₂O₅: 5 MoO₃
 M₈: 10 CaF₂-30 PbO-52 P₂O₅: 8 MoO₃
 M₁₀: 10 CaF₂-30 PbO-50 P₂O₅: 10 MoO₃
 M₁₂: 10 CaF₂-30 PbO-48 P₂O₅: 12 MoO₃
 M₁₅: 10 CaF₂-30 PbO-45 P₂O₅: 15 MoO₃
 M₂₀: 10 CaF₂-30 PbO-40 P₂O₅: 20 MoO₃

The methods of preparation of the samples are similar to those reported in our earlier papers.³³⁻³⁵ The paramagnetic susceptibility of MoO₃ doped CaF₂-PbO-P₂O₅ glasses was determined by Guoy's method at room temperature. In this method the fine powder of the glass sample is taken in a long glass tube of uniform cross section. The tube is suspended to a sensitive digital balance, which can measure the weight up to an accuracy of 0.0001 g. The lower end of the tube is placed in the middle of two strong electromagnetic poles. The strength of the magnetic field is slowly increased and the change in weight Δmg for each field strength (measured up to an accuracy of ± 1 mT) has been determined. Using this Δmg , the volume susceptibility of the samples χ_v was evaluated using the conventional formula. The optical absorption spectra of the glasses were recorded using a CARY 5E UV-VIS-NIR Spectrophotometer in the wavelength range 250–1000 nm. The electron spin resonance spectra of CaF₂-PbO-P₂O₅ glasses doped with molybdenum oxide were recorded at room temperature using commercial X-Band microwave spectrometer Model JEOL JES-TES100 of 100 kHz field modulation.

RESULTS AND DISCUSSION

P₂O₅ is a well-known strong glass forming oxide, participates in the glass network with PO₄ structural units. One of the four oxygen atoms in PO₄ tetrahedron is doubly bonded to the phosphorus atom with the substantial π -bond character to account for pentavalency of phosphorous. The PO₄ tetrahedrons are linked together with covalent bonding in chains or rings by bridging oxygens. Neighbouring phosphate chains are linked together by cross bonding between the metal cation and two non-bridging oxygen atoms of each PO₄ tetrahedron; in general, the P–O–P bond between PO₄ tetrahedra is much stronger than the cross bond between chains via the metal cations.³⁶ Similar to fluoro borate glass network, the phosphate glass network containing alkali-earth fluorides like CaF₂ may consist of P (O, F)₄ or PO₃F or PO₂F₂ units.^{37,38}

PbO in general is a glass modifier and enters the glass network by breaking up the P–O–P (normally the oxygens of PbO break the local symmetry while Pb²⁺

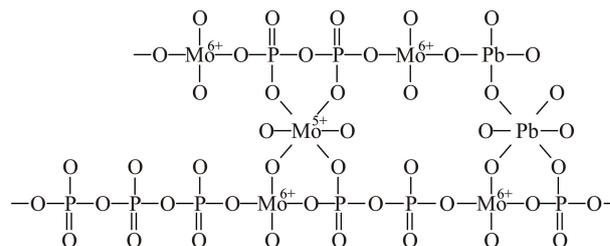


Figure 1. An illustration of positions of molybdenum ions in the phosphate glass network.

ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions. In this case the lead ions are octahedrally positioned. To form octahedral units, Pb should be sp³d² hybridized (6s, 6p and 6d orbitals).^{39,40} However, PbO may also participate in the glass network with PbO₄ structural units when lead ion is linked to four oxygens in a covalency bond configuration. In such a case the network structure is considered to build up from PbO₄ and PO₄ pyramidal units, with P–O–Pb linkages.

Molybdenum ions are expected to exist mainly in the Mo⁶⁺ state in the present CaF₂-PbO-P₂O₅ glass network. However, the reduction of Mo⁶⁺ state to the Mo⁵⁺ state is viable during melting and subsequent annealing process. Our visual examination showed that as the mole fraction of MoO₃ is increased especially up to 15 %, the color of the glass became increasingly brown, indicating a progressive increase in the reduction of molybdenum ions from the Mo⁶⁺ state to the Mo⁵⁺ state. These Mo⁵⁺ ions are quite stable and occupy octahedral positions with distortions due to the Jahn-Teller effect.^{41,42} Earlier ESR studies on the glasses containing molybdenum ions have identified that, Mo^V ions present in octahedral coordination with distorted octahedrons approaching tetragons.^{43,44} The Mo⁶⁺ ions are expected to participate in the glass network as tetrahedral MoO₄²⁻ structural units. Based on the above discussion anticipated positions of molybdenum ions in the phosphate glass network are illustrated in the Figure 1.

From the measured values of density ρ and calculated average molecular weight \bar{M} , various physical parameters such as molybdenum ion concentration N_i and mean molybdenum ion separation r_i of these glasses are evaluated using the conventional formulae and are presented in Table 1.

The values of the magnetic susceptibility (χ) measured at room temperature for all the glasses under investigation are presented in Table 2; the value of χ is found to increase gradually with increase in the concentration of MoO₃. From the measured values of χ , the concentration of Mo⁵⁺ ions (N') is estimated by taking the value of magnetic moment as 1.7 μ_B . The ratio (C), N' /total molybdenum ion concentration (N_i), is estimated

Table 1. Physical parameters of $\text{CaF}_2\text{-PbO-P}_2\text{O}_5\text{: MoO}_3$ glasses

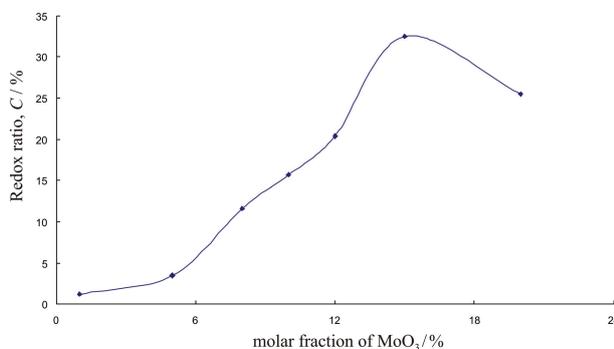
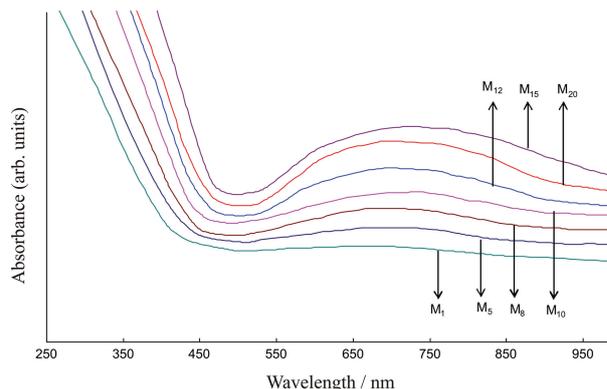
Glass	Avg. mol. wt. $\bar{M}_r / \text{g mol}^{-1}$	Density $\rho / \text{g cm}^{-3}$	Total Mo ion conc. $(N_i / 10^{23} \text{cm}^{-3})$	Inter ionic distance $r_i / \text{\AA}$
M ₀	159.93	4.8416	-	-
M ₁	159.95	4.8657	0.18	3.79
M ₅	160.03	4.9624	0.93	2.20
M ₈	160.09	5.0349	1.52	1.88
M ₁₀	160.13	5.0833	1.91	1.74
M ₁₂	160.17	5.1316	2.31	1.63
M ₁₅	160.23	5.2041	2.93	1.51
M ₂₀	160.33	5.3250	3.99	1.36

Table 2. Data on magnetic properties of $\text{CaF}_2\text{-PbO-P}_2\text{O}_5\text{: MoO}_3$ glasses

Glass	Magnetic Susceptibility $\chi / 10^{-5} \text{e.m.u.}$	Mo ⁵⁺ ion conc. $N' / 10^{22} \text{cm}^{-3}$	Redox Ratio $C (N'/N_i)$
M ₁	0.461	0.02	0.012
M ₅	2.349	0.33	0.035
M ₈	3.812	1.76	0.116
M ₁₀	4.809	3.01	0.157
M ₁₂	5.825	4.72	0.204
M ₁₅	7.381	9.54	0.325
M ₂₀	10.063	10.20	0.255

from the values of N' and furnished in the Table 2. The value of C is observed to increase significantly with increase in the mole fraction of MoO_3 up to 15 %, and beyond this the value of C is observed to decrease considerably (Figure 2).

The optical absorption spectra (Figure 3) of $\text{CaF}_2\text{-PbO-P}_2\text{O}_5\text{: MoO}_3$ glasses were recorded in the wavelength region 250–1000 nm. From the observed absorption edges, we have evaluated the optical band gaps (E_0) of these glasses by drawing Urbach plot (Figure 4). The value of optical band gap is found to decrease with

**Figure 2.** Variation of redox ratio (C) with the conc. of MoO_3 .**Figure 3.** Optical absorption spectra of $\text{CaF}_2\text{-PbO-P}_2\text{O}_5\text{: MoO}_3$ glasses.

increase in the mole fraction of MoO_3 from 1.0 to 15 mol % and for further increase, it is found to increase. Additionally, the spectra of the glasses show a broad absorption band in the region 600–800 nm; a gradual increase in the intensity of this band is observed with increase in the mole fraction of MoO_3 from 1.0 to 15 %. This broad absorption band is attributed to the excitation of $\text{Mo}^{5+} (4d^1)$ ion.⁴⁵ In fact, for this ion, two optical excitations were predicted starting from $b_2 (d_{xy})$ ground state to (d_{xz-yz}) and $(d_{x^2-y^2})$ with $\delta = 15000 \text{cm}^{-1}$ and $\Delta = 23000 \text{cm}^{-1}$.⁴⁵ Perhaps, due to inter charge transition transfer ($\text{Mo}^{5+} \leftrightarrow \text{Mo}^{6+}$) in the glass network, the resolution of these transitions could not be observed. The highest intensity of this band observed in the spectrum of glass M₁₅ points out that the presence of the highest concentration of Mo^{5+} ions in these glasses. Such Mo^{5+} ions may form $\text{Mo}^{5+}\text{O}^{3-}$ molecular orbital states and are expected to participate in the depolymerisation of the glass network^{46–49} creating more bonding defects and non-bridging oxygens (NBO's). Normally, the oxygens of $\text{Mo}^{5+}\text{O}^{3-}$ complexes break the local symmetry while molybdenum ions go in to the interstitial positions. Hence the gradual increase in the concentration of mo-

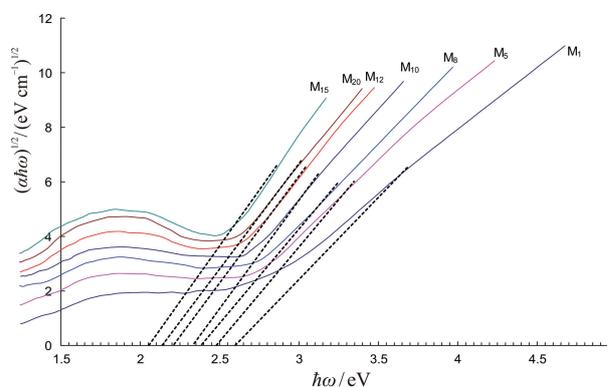
**Figure 4.** Urbach plots to evaluate optical band gaps for $\text{CaF}_2\text{-PbO-P}_2\text{O}_5\text{: MoO}_3$ glasses.

Table 3. Data on ESR spectra of CaF₂-PbO-P₂O₅: MoO₃ glasses

Glass	g_{\parallel}	g_{\perp}	Half-width $\Delta B_{1/2}$ / mT	parameter d / nm
M ₁	1.884	1.945	3.7	0.55
M ₅	1.880	1.941	5.5	0.63
M ₈	1.877	1.937	6.2	0.65
M ₁₀	1.874	1.933	7.3	0.68
M ₁₂	1.869	1.931	7.9	0.71
M ₁₅	1.865	1.924	8.7	0.74
M ₂₀	1.867	1.928	7.5	0.69

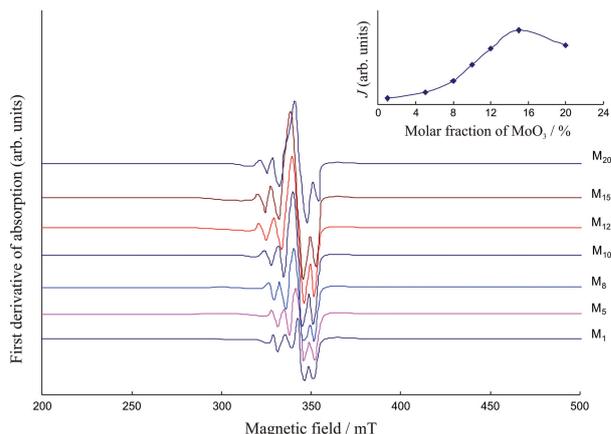
Table 4. ESR parameters of Mo⁵⁺ ions in some disordered compounds

Glass composition	g_{\perp}	g_{\parallel}
CaF ₂ -PbO-P ₂ O ₅ : MoO ₃	1.934	1.874
Li ₂ O-MoO ₃ -P ₂ O ₅	1.933 ^(a)	1.877 ^(a)
MoO ₃ -B ₂ O ₃	1.974 ^(b)	1.940 ^(b)
PbO-Sb ₂ O ₃ -B ₂ O ₃ : MoO ₃	1.930 ^(c)	1.872 ^(c)
MoO ₃ film	1.938 ^(d)	1.890 ^(d)

^(a) Ref. 51, ^(b) Ref. 44, ^(c) Ref 23, ^(d) Ref, 52.

lybdenum ions in the glass network, causes a creation of large number of donor centers; subsequently, the excited states of localized electrons originally trapped on Mo⁵⁺ sites begin to overlap with the empty 3d states on the neighboring Mo⁶⁺ sites. As a result, the impurity band becomes more extended into the main band gap. This development shifts the absorption edge to low energy side, resulting a significant shrinkage in the band gap. This may explain the decrease in the optical band gap with increase in the mole fraction of MoO₃ from 1.0 to 15 %.

The existence of molybdenum ions in Mo⁵⁺ state in these glasses is further confirmed by ESR spectral studies. The ESR spectra (Figure 5) of these glasses consist of a main central line surrounded by less intense satellites. The central line arises from even molybdenum isotopes ($I = 0$) where as satellite lines correspond to the hyper fine structure from odd ⁹⁵Mo and ⁹⁷Mo ($I = 5/2$) isotopes.⁵⁰ The considerable intensity of the signal observed in the spectra of all the glasses, suggests an increasing concentration of Mo⁵⁺O³⁻ complexes. The values of g_{\perp} and g_{\parallel} from these spectra have been evaluated and furnished in Table 3; the structural disorder arising from the site-to-site fluctuations of the local surroundings of the paramagnetic Mo⁵⁺ ions can be accounted for the two components of the g values. Further, the g values obtained for these glasses are found to be consistent with the reported values for many other

**Figure 5.** ESR spectra of CaF₂-PbO-P₂O₅: MoO₃ glasses. Inset gives variation of the intensity of the central line with the concentration of MoO₃.

glass systems containing molybdenum ions (Table 4).

The intensity (J) of the EPR signal is assumed to be proportional to the product of the peak-to-peak height (J) and the square of its width (ΔB):⁵³

$$J \sim I(\Delta B)^2 \quad (1)$$

The dependence of this factor, for the central line with the concentration of MoO₃ is shown as an inset of Figure 5; the figure shows that the intensity of the resonance signal increases with increase in the mole fraction of MoO₃ up to 15 %. This is attributed to the increase in the concentration of Mo⁵⁺ ions in the glass network (as is also evidenced from optical absorption studies).

The intensity and the half width $\Delta B_{1/2}$ of the signal are found to increase with increase in the concentration of MoO₃. For dipolar interactions between paramagnetic ions, the half-width (in Tesla) of the signal is given by,^{54,55}

$$2\Delta B_{1/2} = 3.62 \frac{\mu_0}{4\pi} \frac{(g_{\perp}^2 + 2g_{\parallel}^2)}{g} \frac{\beta}{d^3} C; \quad (2)$$

here g is the mean g -value. From this equation we have calculated the minimal distance d between two molybdenum ions (with the values of reduction factor C from Table 2) and presented in Table 3; these distances are observed to be comparable to the Mo–O–Mo distance in several compounds.⁵² From these calculated distances we conclude that the molybdenum-oxygen polyhedra in glass do not share their edges. This conclusion is consistent with the generally accepted random network model, according to which glass is formed of corner-sharing coordination polyhedral.⁵⁴

Based on molecular orbital theory, the components of g -tensor are given approximately

$$g_{\parallel,\perp} = g_e - \frac{n_{\parallel,\perp} \lambda_{\parallel,\perp}}{D} \quad (3)$$

(with $n_{\parallel} = 8$, $n_{\perp} = 2$ and $D = \delta$ or Δ) if the spin orbit coupling constants are replaced by the corresponding covalent reduction factors k_{\parallel} and k_{\perp} as,⁴⁶

$$\lambda_{\parallel,\perp} = k_{\parallel,\perp}^2 \lambda_0 \quad (4)$$

The k_{\parallel} and k_{\perp} values have been calculated with the free ion spin orbit coupling constant $\lambda_0 = 1030 \text{ cm}^{-1}$.³⁹ The values of k_{\parallel} (=0.56) and k_{\perp} (= 0.68) obtained for the present glasses indicate that the Mo^{5+} ions are linked with less covalency in the present glass matrix.⁵⁶ Further, the differences in the k -values suggest that the Mo–O bonding is less covalent in the perpendicular plane than along z-axis.

The magnetic susceptibility for these glasses arises due to $\text{Mo}^{5+}(4d^1)$ paramagnetic ions. The increase in the value of redox ratio C (obtained from magnetic susceptibility measurements), with increase in the mole fraction of MoO_3 (from 1.0 to 15 %), indicates a gradual increase in the reduction of molybdenum ions from Mo^{6+} state to Mo^{5+} state in the glass matrix. However, we have observed a low value of reduction factor for the glass M_{20} (when compared with that of M_{15}); this observation indicates that molybdenum ions present in Mo^{6+} state in larger concentrations that occupy tetrahedral positions with MoO_4 structural units, in this glass.

CONCLUSION

The summary of the conclusions drawn from various studies of $\text{CaF}_2\text{-PbO-P}_2\text{O}_5$ glass doped with MoO_3 is as follows: The magnetic susceptibility measurements show increasing values of redox ratio of molybdenum ions from Mo^{6+} state to Mo^{5+} with increasing mole fraction of MoO_3 up to 15 %. Optical absorption measurements in the range 250–1000 nm and ESR spectral studies also indicated an increasing concentration of Mo^{5+} ions that occupy octahedral positions with increasing content of MoO_3 up to 15 % mole ratio in the glass matrix.

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SAŽETAK

Magnetske i spektroskopske studije molibdenovih iona u $\text{CaF}_2\text{-PbO-P}_2\text{O}_5$ sustavu stakla

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$\text{CaF}_2\text{-PbO-P}_2\text{O}_5$ stakla koja sadrže različite molarne udjele MoO_3 (u rasponu od 1.0 do 20 %) su pripravljene. Magnetska susceptibilnost, ESR i optička apsorpcija, studije spektara na ovim staklima su bile provedene. Zanimljive promjene promatrane u ovim svojstvima variranjem molarnog udjela MoO_3 su prodiskutirane u pogledu različitih oksidacijskih stanja molibdenovih iona.