EPR and Optical Studies of Mo$^{5+}$ Ions in Lithium Molybdoborate Glasses*

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Abstract. Electron paramagnetic resonance (EPR) and optical absorption studies of Li$_2$O–MoO$_3$–B$_2$O$_3$ with varying concentrations of Li$_2$O, MoO$_3$, and B$_2$O$_3$ have been carried out at room temperature. Two series of glasses, one with constant MoO$_3$ (CM) and another with constant borate (CB), have been investigated. Characteristic EPR spectra of Mo$^{5+}$ have been observed centered around $g \approx 2.00$, which are attributed to Mo$^{5+}$ ion in an octahedral coordination sphere with an axial distortion. The spectra also show strong dependence on the concentration of Li$_2$O and B$_2$O$_3$. Spin concentrations ($N$) and magnetic susceptibilities ($\chi$) have been calculated. In the CM series, the $N$ values decrease with increasing Li$_2$O content up to 30 mol%, while in the CB series variation of $N$ is found to increase initially up to 20 mol%, and with further increase in the Li$_2$O content the $N$ values tend to decrease. The variation of magnetic susceptibilities is almost similar to that observed with the variation of $N$. From the optical absorption spectra, an absorption edge ($a$) has been evaluated. In the CM series, the values of $a$ show a blueshift. On the other hand, in the CB series a redshift is observed. The observed variations in spectral parameters are explained by considering the molybdoborate network. Addition of Li$_2$O to the CM and CB series results in modification of [MoO$_{3.5}$]$^6$–$[\text{MoOO}_3]$ and [BO$_{3.5}$]$^6$–[BO]–[BOO] groups, respectively, leading to creation of nonbridging oxygens. The optical basicity of the glasses has been evaluated in both the CM and the CB glasses. The optical basicity can be used to classify the covalent-to-ionic ratios of the glass, since an increasing optical basicity indicates decreasing covalency. It is observed that the covalency between Mo$^{5+}$ ions and oxygen ligands increases in the CB series, whereas in the CM series the covalency between Mo$^{5+}$ ions and oxygen ligands decreases.

1 Introduction

Transition-metal oxides, when melted in appropriate amounts with a basic glass former, form a glass in which the transition-metal ion exists in different valence

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states [1]. Molybdenum trioxide is a well-known glass former [2] in which molybdenum exists as Mo$^{5+}$ (4d$^1$ electron). It is essentially a small polaron hopping from a Mo$^{5+}$ to a Mo$^{6+}$ site and as a result, the glasses containing MoO$_3$ are n-type semiconductors [3]. Lithium boromolybdate glasses may be used as positive electrodes in solid-state batteries, their electrical conductivity being mainly due to both the high mobility of the lithium ion and electron semiconduction due to the electron transfer, or hopping of unpaired electrons from the paramagnetic Mo$^{5+}$ ions to the diamagnetic Mo$^{6+}$ ions [4]. MoO$_3$-containing glasses are also used for the development of optical and radiation glasses and crystalline glass materials [5].

The nature and extent of structural inhomogeneity in glass is one of the principal subjects of the general problem of glass structure [6]. There have been reports in the literature on phosphate glasses containing molybdenum because of their special electrical properties, but there is not much information regarding borate glasses containing molybdenum. In the present work, molybdenum-based alkali–borate glasses have been investigated. We employ electron paramagnetic resonance (EPR) and optical studies to obtain detailed information about the local structure and the extent of interaction between adjacent molybdenum sites in respective glasses as a function of the MoO$_3$ and Li$_2$O concentration.

2 Experimental

The glass samples were prepared by the conventional melt-quenching method using analytical-reagent grade Li$_2$CO$_3$, H$_2$BO$_3$ and MoO$_3$. Calculated quantities of initial materials were mixed well by grinding them together to a fine powder. The powders were heated in porcelain crucibles in an electric furnace (Heat globe, Bangalore) to decompose certain materials. The batches were then melted in the temperature range of 1000–1300 K for about 10 min in a furnace, stirred to ensure homogeneity, and quenched between brass blocks kept at room temperature. The glasses with high lithium content are transparent, while those with high molybdenum content are colored. The glasses were then annealed below their glass-transition temperature. Since the number of spins participating in the resonance is greatly changed by the modification of the matrix composition, two series of glasses were prepared with the general formula (i) $x$Li$_2$O – 10MoO$_3$ – (100 – $x$)B$_2$O$_3$ for constant molybdate (CM) series and (ii) $x$Li$_2$O – (40 – $x$)MoO$_3$ – 60B$_2$O$_3$ for constant borate (CB) series, where $x$ is varied from 5 to 35 mol%.

The amorphous nature of the samples was confirmed by X-ray diffraction (XRD) (JEOL JOX-8P X-ray diffractometer). The EPR spectra were recorded on an EPR spectrometer (JEOL FE-1X) operating in the X-band (ca. 9.200 GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 500 mT and the microwave power was maintained at 5 mW. A powdered glass sample of 100 mg was placed in a quartz tube for EPR measurements. The optical absorption spectra of the glasses were recorded using a
JASCO ultraviolet-visible-near infrared spectrophotometer operating in the wavelength region of 300–900 nm.

3 Results and Discussion

3.1 XRD

The XRD pattern of an amorphous material is distinctly different from that of a crystalline material. In the present study, the XRD patterns of all the glasses did not show any sharp peaks. Broad humps have been observed which are characteristic features of amorphous materials.

3.2 EPR Studies

Figures 1 and 2 represent the types of EPR spectra observed in the CM and CB series. EPR spectra exhibit resonance signals similar to those reported for Mo$^{5+}$ ions in other glass systems [4, 5, 7–13]. Some EPR spectra, shown in Fig. 1 and 2, consist of a main central line around $g \approx 1.986$ surrounded by less intense satellite lines. The line shape of the central $I = 0$ resonance signal suggests an axially symmetric g-matrix, the satellite lines correspond to the hyperfine structure from odd $^{95}$Mo and $^{97}$Mo isotopes ($I = 5/2$, natural abundance of 15.78% and 9.69%, respectively) indicating that the Mo$^{5+}$ cation in the molybdoborate-based glasses studied has an octahedral coordination [11–12] with a weak axial distortion.

The dependence of the resonance line intensity and particularly the number of spins $N$ upon the MoO$_3$ concentration differs for the two series of glasses. In the CM series the EPR spectra show significant changes both in the number of spins and the glass structure itself (Figs. 1 and 3). The increase in the alkali oxide content results in a decrease of the number of spins leading to a minimum of the intensity of the EPR signal for the diborate composition (30 mol%). When the alkali oxide concentration exceeds 30 mol%, the value of $N$ slowly increases. Concurrent with the change in the EPR signal intensity, the line shape itself changes markedly. As can be seen from Fig. 1, the weak hyperfine splitting spectrum is observed in all the glasses with varying intensity. Initially the signal intensity increases up to the alkali concentration of 15 mol%, and thereafter it decreases till the concentration of 30 mol%, and then increases when the alkali content is greater than 30 mol%. Similarly in the CB series, the weak hyperfine splitting is not observed for MoO$_3$ content of 5 and 10 mol%. However, at 15 mol%, it was observed and the resolution of the splitting increases. The intensity of the observed signal increases with increasing concentration of MoO$_3$ and attains a maximum value at 20 mol%, decreasing thereafter. It is interesting to note that the line width increases with the MoO$_3$ content. Thus, the shape of the EPR signal is modified with variation of the glass composition.
3.3 Calculation of Spin Concentration

The number of spins $N$ participating in resonance can be calculated by comparing the area under the absorption curve of the sample with known concentration (CuSO$_4$·5H$_2$O in this study). Weil et al. [14] gave the following expression, which includes the experimental parameters of both the sample and the standard:
Fig. 2. EPR spectra of the CB glass series $x$Li$_2$O – (40 – $x$)MoO$_3$ – 60B$_2$O$_3$ (10 ≤ $x$ ≤ 35 mol%): 35 (a), 30 (b), 25 (c), 20 (d), 15 (e), 10 mol% (f).

$$N_2 = \frac{A \cdot (\text{scan})^2 G_{std} (B_{m})_{std} (g_{std})^2 [S(S+1)]_{std} (P_{std})^{1/2}}{A_{std} \cdot (\text{scan}_{std})^2 G_x (B_{m})_x (g_x)^2 [S(S+1)]_x (P_x)^{1/2}} [\text{std}],$$

where $A$ is the area under the absorption curve which can be obtained by double integrating the first derivative EPR absorption curve, scan is the magnetic field per unit length of the chart, $G$ is the gain, $B_m$ is the modulation amplitude, $g^2$ is the anisotropic transition probability, $S$ is the electron spin of the system in its ground state and $P$ is the power of the microwave source. The subscripts $x$ and
Fig. 3. Variation of $N$ in $x\text{Li}_2\text{O} - 10\text{MoO}_3 - (100 - x)\text{B}_2\text{O}_3$ glass as a function of the $\text{Li}_2\text{O}$ content.

std represent the corresponding quantities for $\text{Mo}^{5+}$ in the glass sample and the reference ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), respectively.

The variation of $N$ in the CM and the CB series is shown in Figs. 3 and 4, respectively. In the CM series, $N$ decreases with increasing $\text{Li}_2\text{O}$ content and reaches a minimum at the concentration of 30 mol%. With a further increase in the $\text{Li}_2\text{O}$ content the value of $N$ increases. Interestingly, in the CB series, a reverse trend is seen in the variation of $N$ reaching a maximum at the concentration of 20 mol% and decreasing thereafter.

Fig. 4. Variation of $N$ in CB glass series as a function of the $\text{Li}_2\text{O}$ content.
3.4 Calculation of Paramagnetic Susceptibility from EPR Data

The EPR data can be used to calculate the paramagnetic susceptibility $\chi$ of the sample by using the following formula [15]:

$$\chi = \frac{N g^2 \beta^2 J (J + 1)}{3 k_B T},$$  \hspace{1cm} (2)

where $N$ is the number of spins per cubic meter, $\beta$ is the Bohr magneton, $J$ is the total angular momentum, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The number of spins $N$ can be calculated by double integrating the first derivative EPR spectrum and $g$ is taken from the EPR data. It is observed that the magnetic susceptibility also follows the trend of $N$ in both systems as indicated in Figs. 5 and 6. We choose to determine the spin susceptibility from EPR because this technique has several advantages over a static measurement, where a diamagnetic contribution must be subtracted.

In molybdenum trioxide, MoO$_3$, the Mo–O bond may be considered as considerably covalent (electronegativity difference between Mo and O is the same as that for Si and O) [16]. Since the coordination number of molybdenum is six, we can consider that MoO$_3$ in molybdoborate glasses provides octahedral structural units of the $M_I$-type ([MoO$_{6/2}$]) necessary for the extensive network formation. B$_2$O$_3$ is made up of planar $B_3$ ([BO$_{3/2}$]) triangles [17]. The structure of molybdoborate glasses may therefore be considered as generated from the corners-shared triangular and octahedral units as shown in Fig. 7. With increasing Li$_2$O content (Fig. 7a), Mo–Mo bonds are broken and the Li$^+$ ion gets attached to O$^-$, so that the charge is balanced. In Fig. 7b, as the concentration of Li$_2$O is

![Graph](image_url)

**Fig. 5.** Variation of $\chi$ in the CM glass series as a function of the Li$_2$O content.
increased in the CM series, the alkali oxide converts the bridging oxygen in a trigonal unit to tetrahedral by creating a nonbridging oxygen (NBO). The Li$^+$ ion occupies O$^-$ in the tetrahedral unit. Therefore, the network structures of these glasses are degraded by addition of Li$_2$O, and the preferential group modification is essentially decided by electronegativity of [BO$_{3/2}$]$^0$ and [MoO$_{6/2}$]$^0$ units. The electronegativities are calculated by the Sanderson procedure [18] and are 2.79 and 3.06 for $B_3$ and $M_1$, respectively.

Li$_2$O is highly ionic and in glasses Li$_2$O ionizes as

$$\text{Li}_2\text{O} \rightarrow 2\text{Li}^+ + \text{O}^{2-}.$$  

**Fig. 6.** Variation of $\chi$ in the CB glass series as a function of the Li$_2$O content.

**Fig. 7.** Modified octahedral and trigonal units depending on the Li$_2$O content. a Li$_2$O content of $<10$ mol%, b Li$_2$O content of $>10$ mol%.
The $\text{O}^{2-}$ ion that is available would be preferentially taken up by the $[\text{MoO}_{6/2}]^0$ leading to the formation of $M_2$ ($[\text{MoOO}_{5/2}]^-$)

$$[\text{MoO}_{6/2}]^0 + \text{O}^{2-} \rightarrow [\text{MoOO}_{5/2}]^-.$$

Since the concentration of MoO$_3$ in the CM series is only 10 mol%, the remaining available O$_{2-}$ ions will be taken up by $[\text{BO}_{3/2}]^0$ to get modified into $B_3$ ($[\text{BO}_{4/2}]^-$). Not all the $B_3$ species, however, can be converted into $B_4$ species by increasing the modifier content. Ideally, if all $B_4$ species are connected to only $B_3$ species and vice versa, the ratio of $B_4$ to $B_3$ in the structure has to be 3:4 or $N_3 = N_4/(B_3 + B_4)$ should reach a saturation value of 3/7, which is approximately 0.43. However, the experimentally observed maximum $N_4$ value is about 0.5 and corresponds to a modifier concentration of 33.3 mol%. In this region where $N_4$ has exceeded the limiting value, $B_2$ ($[\text{BO}_{4/2}O]^-$) species are formed in the place of $B_4$, and some of the existing $B_4$ are induced to undergo structural rearrangement to $B_2$. Therefore, in the CM and the CB series, when the modifier concentration exceeds 33.3 mol%, the extended three-dimensional structure breaks down, and reconversion of $B_4$ to $B_3$ takes place. This causes the $N$ value to decrease initially and then to increase.

The dependence of the EPR signal, the value of $N$ and the magnetic susceptibility on the molybdenum oxide content in the CB series indicates that at higher concentration the number of Mo$^{5+}$ ions decreases. This fact may be due to formation of strongly antiferromagnetically coupled binuclear oxo-bridged Mo$^{5+}$ ions. This assumption is plausible in the view of the ability of molybdenum readily to form Mo–Mo bonds [19], and thus one could explain the conversion of paramagnetic substances into diamagnetic substance Mo$^{6+}$ [20–22]. The variation may be due to the structural changes with composition and the modification of the boron network with alkali content.

### 4 Optical Absorption Studies

The optical absorption spectra of Mo$^{5+}$ ions in the CM and CB glasses at 300 K have been recorded in the wavelength region of 300–900 nm and are shown in Figs. 8 and 9, respectively. The general feature of these spectra is that they are all composed of a flat baseline and a steep cutoff. However, it is interesting to observe that the ultraviolet absorption band edge of these glasses in case of CM series shifts from a value of 411 to 338 nm, thus exhibiting a blueshift. On the other hand, an increase of the molybdenum content in the CB system yields an apparent band edge shift from a value of 330 to 696 nm, exhibiting a redshift. This shift is attributed to large Mo$^{5+}$ absorption occurring in this region of the spectrum.

#### 4.1 Optical Basicity of the Glass

The optical basicity ($A_{ib}$) of an oxide glass reflects the ability of the glass to donate a negative charge to the probe ion [23]. Duffy and Ingram [24] reported
that the ideal values of optical basicity could be predicted from the composition of the glass and the basicity-moderating parameters of the various cations present. The theoretical values of optical basicity of the glass can be estimated using the formula [24]

\[ A_{th} = \sum_{i=1}^{n} \frac{Z_i f_i}{2\gamma_i} \]

Fig. 8. Optical absorption spectra of Mo\(^{5+}\) ions in the CM glass series as a function of the Li\(_2\)O content: 1, 10 mol%; 2, 15 mol%; 3, 20 mol%; 4, 25 mol%; 5, 30 mol%; 6, 35 mol%. Blueshift is observed with increasing Li\(_2\)O content (or the MoO\(_3\) content keeping constant).

Fig. 9. Optical absorption spectra of Mo\(^{5+}\) ions in the CB glass series as a function of the MoO\(_3\) content: 1, 5 mol%; 2, 10 mol%; 3, 15 mol%; 4, 20 mol%; 5, 25 mol%. Redshift is observed with decreasing Li\(_2\)O content (or with increasing MoO\(_3\) content).
where $n$ is the total number of cations present, $Z_i$ is the oxidation number in the $i$th cation, $r_i$ is the ratio of the number of $i$th cations to the number of oxides present and $g_i$ is the basicity-moderating parameter of the $i$th cation. The basicity-moderating parameter $g_i$ can be calculated from the following equation:

$$g_i = 1.36(x_i - 0.26),$$

where $x_i$ is the Pauling electronegativity [25] of the cation. The theoretical values of optical basicity were calculated for all the glass samples and are shown in Fig. 10. It is interesting to observe that the optical basicity decreases with increasing molybdenum content (CB series), whereas it increases in the CM series. The optical basicity can be used to classify the covalent-to-ionic ratios of the glass, since an increasing optical basicity indicates decreasing covalency. In the present study it is observed that the optical basicity decreases linearly with the MoO$_3$ content, indicating that the covalency between Mo$^{5+}$ ions and oxygen ligands increases in the CB series, whereas in the CM series the covalency between Mo$^{5+}$ ions and oxygen ligands decreases with increasing Li$_2$O content.

### 5 Conclusions

The EPR spectra of molybdenum ions in the CM and the CB series consist of a main central line at $g \approx 1.986$ surrounded by less intense satellite lines indicating that the Mo$^{5+}$ cation in the lithium molybdoberate glasses studied has an octahedral coordination with a weak axial distortion. The number of spins participating in the resonance $N$ and the paramagnetic susceptibilities $\chi$ for the two series
exhibit different dependences on the molybdenum oxide concentration. In the CM
series, $N$ and $\chi$ decrease with increasing Li$_2$O content and reach a minimum at
the concentration of 30 mol%, and thereafter the value of $N$ increases. Interest-
ingly, in the CB series, a reverse trend is observed for $N$ and $\chi$, reaching a maxi-
mum at the concentration of 20 mol% and thereafter decreasing. The observed
variations in the spectral parameters are explained by considering the molybdo-
borate network. Addition of Li$_2$O in the CM and CB series results in the modi-
fication of [MoO$_{6/2}$]$^0$ → [MoOO$_{5/2}$]$^- $ and [BO$_{3/2}$]$^0$ → [BO$_{4/2}$]$^- $ → [BOO$_{2/2}$]$^- $ groups,
respectively, leading to the creation of NBOs. In the CM series, the ultraviolet
band edges show a blueshift, and in the CB series a redshift is observed. This
shift is attributed to large Mo$^{5+}$ absorption occurring in this region of the spec-
trum. It is also observed that the optical basicity decreases linearly with the MoO$_3$
content, indicating that the covalency between Mo$^{5+}$ ions and oxygen ligands in-
creases in the CB series, whereas in the CM series the covalency between Mo$^{5+}$
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