Structure-property studies in \((0.8-x)\text{MoO}_3-0.2\text{B}_2\text{O}_3-x\text{K}_2\text{O}\) \((0 \leq x \leq 0.25)\) glasses by spectral and magnetic measurements

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Glasses of the \((0.8-x)\text{MoO}_3-0.2\text{B}_2\text{O}_3-x\text{K}_2\text{O}\) \((0 \leq x \leq 0.25)\) system \((S1-S6: x = 0, 0.05, 0.10, 0.15, 0.20, 0.25)\) have been prepared by air quenching the melt in the range 1073-1173 K. Glassy phase has been ascertained by powder X-ray diffraction patterns of the samples. Differential thermal analysis results show the glass transition temperature in the range 573-673 K. Infrared spectral results at 300 K show the presence of octahedral \([\text{OMoO}_6]\), tetrahedral \([\text{BO}_4]\) and trigonal \([\text{BO}_3]_2\) and \(n\) free oxygen containing trigonal \([\text{BO}_{3+n/2}]^n\) \((n = 1,2,3)\) units. The calculated values of the magnetic susceptibilities (~10\(^{-5}\) emu/G) from magnetic moment data at 300 K show the weak paramagnetic nature of the glasses. The magnitude of the calculated exchange integrals of the small polaron is found to be in the range 0.003-0.058 eV (~10\(^{-11}-10^{-12}\) Hz). The observed electron paramagnetic resonance results show that the lineshapes vary from axially symmetric in binary \(S1(x = 0)\) to isotropic in ternary compositions \(S2(x=0.05)-S6(x = 0.25)\) at 300 and 77 K. Negative g-shift indicates that the paramagnetic site \(\text{Mo}^{5+}(4d^3)\) exists as molybdenyl, MoO\(^5+\), ion in the glasses. The partially resolved hyperfine structures indicate that the small polaron hopping depends on temperature as well as on the glass network. Appreciable difference in the values of g- and A-interaction matrices between \(S1(x = 0)\) and \(S2(x = 0.05)-S6(x = 0.25)\) shows distinct difference in the network structures of the binary and ternary compositions.

Keywords: Structure activity relationships, Glasses, Magnetic properties, EPR spectroscopy, IR spectroscopy

Molybdenum trioxide, MoO\(_3\), forms glasses\(^{1-8}\) fairly easily in which Mo is known to exist in \(\text{Mo}^{5+}(4d^4)\) and \(\text{Mo}^{6+}(4d^3)\) states\(^{5,7,9}\). These glasses are known to contain \([\text{MoO}_6]\) or \([\text{OMoO}_5]\) groups\(^{10}\) in the glass network. Due to thermal excitation the \(\text{Mo}^{5+}(4d^3)\) unpaired electron, which is essentially a small polaron\(^{11,12}\), hops from a \(\text{Mo}^{5+}\) site to a \(\text{Mo}^{6+}\) site. As a result, molybdate glasses are n-type semiconductors\(^{9,10,13-15}\). Boron trioxide, B\(_2\)O\(_3\), is also known to form borate glasses\(^1\) easily. The network structure of pure B\(_2\)O\(_3\) is known to consist of predominantly connected boroxol rings built up of only triangular \([\text{BO}_3]_2\) units\(^{16,17}\). However, in the presence of network modifier such as alkali metal oxides, the borate glass structure contains trigonal \([\text{BO}_3]_2\), tetrahedral \([\text{BO}_4]_2\) units\(^{17-19}\) as well as trigonal \([\text{BO}_3]_n\) units\(^{16}\) containing one to three non-bonding oxygens depending on the concentrations of the modifier metal oxide. Since a ternary system such as \(\text{MoO}_3\cdot\text{B}_2\text{O}_3\cdot\text{K}_2\text{O}\) contains different structural units with interesting paramagnetic probe, \(\text{Mo}^{5+}(4d^3)\), the study of structure–property relations as well as site symmetry around the \(\text{Mo}^{5+}\) site of such systems is indeed interesting. However, the reports on EPR studies of such systems\(^5,20-24\) are limited.

In the present study, we report the structure-property relationships in the binary/ternary \((0.8-x)\text{MoO}_3-0.2\text{B}_2\text{O}_3-x\text{K}_2\text{O}\) \((0 \leq x \leq 0.25)\) glasses by IR spectroscopy and magnetic susceptibility at 300 K and EPR results at 300 and 77 K.

Materials and Methods

Batches for each glass containing calculated amounts of reagent grades ammonium molybdate [(NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\)4H\(_2\)O], boric acid, H\(_3\)BO\(_3\), and potassium carbonate, K\(_2\)CO\(_3\), as sources of MoO\(_3\), B\(_2\)O\(_3\), and K\(_2\)O, respectively, in situ were melted in silica crucibles in the range 1073-1173 K and air quenched between two dry ice cold aluminium plates to prepare the glasses. The glassy phase in the samples was ascertained by powder x-ray diffraction (XRD) patterns\(^{25}\). The powder XRD patterns of the samples were obtained in a Rikagu Miniflex X-ray diffractometer using Cu K\(_\alpha\) radiation (\(\lambda=1.5405\) Å) at a scan rate of 2° per minute in the 2θ range of 5° - 80° in The power, counts per second and time constant were 30 kV/10 mA, 500 and 1 s, respectively. Density measurements were made by liquid displacement method using carbon tetrachloride as the standard liquid (density 1.594 g/cc at room
Results and Discussion

XRD studies

Powder XRD patterns of the samples S1-S6 (Fig. 1) without any characteristic diffraction peak indicate the formation of glassy phase in the samples. The DTA traces show the glass transition temperature ($T_g$) around 623, 613, 628, 643, 648 and 673 K, respectively in the glasses S1-S6. Apart from the transition at $T_g$ no other phase transition such as crystallization temperature of the glasses are indicated prominently in the DTA traces. The observed densities (Table 1) are found to be slightly less than that of the molybdophosphate glasses and a slightly decreasing trend is observed with decreasing MoO$_3$ content. The concentrations of Mo$^{5+}(4d^7)$ ions are found to be consistently less than those of Mo$^{6+}$ ions (Table 1) in the glasses, since the Mo$^{5+}$ ions are generated by reduction of Mo$^{6+}$ ions during the melting process and exist as lattice defects. Using the results of chemical analyses we have calculated the small polaron radius ($r_p$) and the average TM ion separation ($R$) in the glasses as reported earlier.

The magnitudes of $r_p$ and $R$ are found to be similar to those of V$_2$O$_5$-containing glasses. Furthermore, the values of $r_p$ and $R$ do not show any regular variation with mol% MoO$_3$ in the glasses. However, only slight variation in the values of $r_p$ and $R$ among S1 and S2-S6 is observed. As discussed in the IR spectral studies vide infra, this variation is attributed to the role of K$_2$O in modifying the binary MoO$_3$-B$_2$O$_3$ glass network (S1) in forming the ternary glasses S2-S6 which in turn are manifested through the variations in the values of $r_p$ and $R$ from binary S1 to ternary S2-S6 glasses.

Infrared studies

The IR spectra of S1-S6 in the range 400-1600 cm$^{-1}$ are shown in Fig. 2. It is known from literature that Mo prefers octahedral coordination in [MoO$_5$H$_2$] or [MoO$_5$O$_2$] units in glassy as well as in polycrystalline network. On the other hand, B$_2$O$_3$-containing glasses exhibit even more complex geometries. Apart from the trigonal [BO$_3$]$_2$ units, the boroxol rings help in the formation of triborate, pentaborate groups and diborate groups also. However, addition of an alkali metal oxide such as K$_2$O leads to the destruction of coordination of boron

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (gm/cm$^3$)</th>
<th>No. of Mo$^{5+}$ ions per gm</th>
<th>No. of Mo$^{6+}$ ions per gm</th>
<th>Small polaron radius, $r_p$ (Å)</th>
<th>Avg. TM ion separation, $R$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>2.972</td>
<td>3.359 $\times 10^{20}$</td>
<td>6.724 $\times 10^{20}$</td>
<td>4.03</td>
<td>7.20</td>
</tr>
<tr>
<td>S2</td>
<td>2.568</td>
<td>3.484 $\times 10^{20}$</td>
<td>6.968 $\times 10^{20}$</td>
<td>3.98</td>
<td>7.12</td>
</tr>
<tr>
<td>S3</td>
<td>2.647</td>
<td>3.553 $\times 10^{20}$</td>
<td>7.100 $\times 10^{20}$</td>
<td>3.95</td>
<td>7.07</td>
</tr>
<tr>
<td>S4</td>
<td>2.559</td>
<td>3.516 $\times 10^{20}$</td>
<td>7.238 $\times 10^{20}$</td>
<td>3.94</td>
<td>7.10</td>
</tr>
<tr>
<td>S5</td>
<td>2.520</td>
<td>3.484 $\times 10^{20}$</td>
<td>7.383 $\times 10^{20}$</td>
<td>3.93</td>
<td>7.12</td>
</tr>
<tr>
<td>S6</td>
<td>2.478</td>
<td>3.691 $\times 10^{20}$</td>
<td>7.527 $\times 10^{20}$</td>
<td>3.89</td>
<td>6.98</td>
</tr>
</tbody>
</table>
forming meta-, pyro- and orthoborate groups\textsuperscript{17,18} as well as “free” tetrahedral [BO\textsubscript{4/2}] units\textsuperscript{16-18} as follows:

\[
\text{[BO}_{3/2}\text{]} \xrightarrow{K_2O} \text{[BO}_{4/2}\text{]} ^- \\
\]

Furthermore, since K\textsubscript{2}O acts a network modifier, it affects the coordination of Mo as follows:

\[
\text{K}_2\text{O} \rightarrow \text{2K}^+ + \text{O}^{2-} \\
\text{Mo–O–Mo+ O}^{2-} \rightarrow \text{2[Mo–O]}^- \xrightarrow{2\text{K}^+} \text{2Mo–O–K} \\
\]

The IR spectra were analysed for the presence of linkages such as Mo–O–Mo, Mo–O, Mo=O, B–O, O–B–O and Mo–O–K as part of the group(s) in the glasses. The shoulder at \(\sim 430\) cm\(^{-1}\) in S2-S6 is due to the K–O stretching vibration in the matrix where K\(^+\) has coordination number of four with respect to the oxygens\textsuperscript{18}. The shoulder at \(\sim 462\) cm\(^{-1}\) is associated with the diborate groups which basically contain tetrahedral [BO\textsubscript{4/2}] groups\textsuperscript{19}. The sharp peak at \(\sim 551\) cm\(^{-1}\) in S1-S4 is attributed to the symmetric bending mode of O–B–O of [BO\textsubscript{3/2}] and [BO\textsubscript{4/2}]\(^-\) units\textsuperscript{19,32}, whereas in S5 and S6, because of the relatively high K\textsubscript{2}O content, more [BO\textsubscript{4/2}] tetrahedral units are formed and this sharp peak at \(\sim 551\) cm\(^{-1}\) is ascribed to the symmetric vibrations\textsuperscript{17,18} of the loose [BO\textsubscript{4/2}]\(^-\) tetrahedral units. The band in the range \(625-680\) cm\(^{-1}\) in S3-S5 is attributed to the bridging oxygens\textsuperscript{17} between the trigonal [BO\textsubscript{3/2}] groups. Nuclear magnetic resonance\textsuperscript{33} studies of B\textsubscript{2}O\textsubscript{3}-containing glasses indicate the presence of boroxol rings in the matrix and the ring breathing modes of six membered borate rings with [BO\textsubscript{4/2}]\(^-\) tetrahedra give rise to bands in the range 752-765 cm\(^{-1}\) in S2-S6. The peak at \(\sim 725\) cm\(^{-1}\) is due to the ring mode\textsuperscript{34} of B–O–B unit which is formed due to the interlinking of the trigonal [BO\textsubscript{4/2}] groups\textsuperscript{18,20} present in the meta- and pyroborate-containing boroxol rings. The vibrations of isolated tetrahedral [MoO\textsubscript{4/2}]\(^-\) groups\textsuperscript{2} occur at \(\sim 760\) cm\(^{-1}\). However, the absence of this band at higher mole% of MoO\textsubscript{3} in S1 and S2 shows that the band in the range 752-765 cm\(^{-1}\) is due to [BO\textsubscript{4/2}]\(^-\) tetrahedra only. This result also shows that with more K\textsubscript{2}O content, the tetrahedral [BO\textsubscript{4/2}]\(^-\) units are further transformed into trigonal [BO\textsubscript{3}]\(^n\) \((n = 1, 2, 3)\) units. However, for clear visualization of the structure of this unit with number of free oxygens, \(n\), we designate it as [BO\textsubscript{4/2-(3-n)x}]\(^n\) \((n = 1, 2, 3)\) unit.

The weak shoulder at \(\sim 820\) cm\(^{-1}\) in S1-S6 is attributed to the bridging Mo–O–Mo group\textsuperscript{2}. The sharp peak/weak shoulder in the range 864-871 cm\(^{-1}\) in S1-S6 is attributed to the symmetric stretching of Mo–O bond in [OMoO\textsubscript{3/2}]\(^-\) unit\textsuperscript{10}. Thus, the band at \(\sim 900\) cm\(^{-1}\) in S4-S6 is due to the B–O stretching mode\textsuperscript{18} of the [BO\textsubscript{3/2}]\(^-\) tetrahedral unit. The shoulder at \(\sim 1033\) cm\(^{-1}\) in S1-S3 which appears as a well defined peak in S4-S5 is also due to the vibration of [BO\textsubscript{4/2}]\(^-\) group\textsuperscript{17}. A very weak peak in S2 and a very sharp peak in the range 1103-1110 cm\(^{-1}\) in S3-S6 may be assigned to the vibrations of the non-bridging oxygens of the trigonal [BO\textsubscript{2/3-(3-n)x}]\(^n\) \((n = 1, 2, 3)\) units\textsuperscript{16,17} in the matrix. As mentioned earlier, these groups are formed by the destruction of the tetrahedral [BO\textsubscript{4/2}]\(^-\) groups by increasing K\textsubscript{2}O content in the matrix. This band is absent in S1 as it does not contain K\textsubscript{2}O. The sharp peak at 1197 cm\(^{-1}\) in S1 is due to the B–O bonds of trigonal [BO\textsubscript{3/2}] unit\textsuperscript{18}. Since trigonal [BO\textsubscript{3/2}] units are converted to tetrahedral [BO\textsubscript{4/2}]\(^-\) units with the addition of K\textsubscript{2}O, the peak at \(\sim 1197\) cm\(^{-1}\) in S1 is relatively smeared out in S2 and S3. However, the reappearance of the peak at 1199 cm\(^{-1}\) in S4, 1201 cm\(^{-1}\) in S5 and at
1201 cm$^{-1}$ in S6 which is merged with a band at 1242 cm$^{-1}$ is due to the stretching of the free B–O of the $[\text{BO}_{3(n+3/2)}]^n(\text{n}=1,2,3)$ units. The peak at ~1242 cm$^{-1}$ in S1-S6 is ascribed to the asymmetric stretching of the $[\text{BO}_{3/2}]$ groups which are either isolated or included in the meta- and pyroborate containing boroxol rings. The shoulder at ~1353 cm$^{-1}$ in S1-S6 is due to the trigonal $[\text{BO}_{3/2}]$ units present in the glasses. The very intense peak in S1-S6 in the range 1440-1465 cm$^{-1}$ is attributed to antisymmetrical stretching vibrations of B–O–B groups which occur in the matrix by interconnecting triangular $[\text{BO}_{3/2}]$ and tetrahedral $[\text{BO}_{4/2}]$ groups.

Magnetic studies

Table 2 shows the calculated values of magnetic susceptibility ($\chi$), Weiss-constant ($\theta$) and the small polaron exchange integral ($j$) from the observed magnetic moment versus magnetic field data at 300 K. The values of $\theta$ were calculated using Curie-Weiss law, while $j$ was evaluated using the relationship, $\theta = 2/3 \, z \, s(s+1)j/k$, where $z$ is the number of next nearest sites available for a polaron to hop, $s$ is the spin and $k$ is the Boltzmann constant. We assume a plausible value of $z$ to be 1 in the random glassy network for our calculations. The fairly low values of $\chi$ indicate weak paramagnetism in these glasses. The values of the Weiss constants and the exchange integrals do not show any regularity with compositions. However, the appreciable magnitudes of the exchange integrals in the range 0.003-0.058 eV (~10$^{11}$-10$^{12}$ Hz) indicate phonon assisted hopping of the Mo$^{5+}$ site within the range of the small polaron radius ($r_p$) in the matrix.

EPR studies

The observed EPR lineshapes of the glasses S1-S6, at 300 and 77 K, are shown in Figs 3 and 4, respectively. In glasses of similar systems, it is known that the Mo$^{5+}$ ($4d^+$) small polaron hops in the lattice from a Mo$^{5+}$ site to a Mo$^{6+}$ site due to thermal excitation. Furthermore, from our earlier temperature dependent EPR studies of the V$_2$O$_5$-containing glasses, it is known that if the thermal hopping rate of the small polaron is fast enough, then the anisotropic hyperfine features of the paramagnetic sites get smeared out and as a result, isotropic lineshapes are observed. However, in the present system, since the binary glass S1 has a network entirely different from those of S2-S6, axially symmetric EPR lineshapes at 300 and 77 K are observed in contrast to the ternary glasses S2-S6, which exhibit isotropic lineshapes with partially smeared out hyperfine structures. This indicates that small polaron hopping depends either on the glass network structure or on the availability of a Mo$^{5+}$ site within the range of the small polaron radius ($r_p$) in the matrix.

Fig. 3—Observed EPR lineshapes of the glasses S1-S6 of (0.8-x)MoO$_3$-0.2B$_2$O$_3$-xK$_2$O (0 \leq x \leq 0.25) system at 300 K.

### Table 2—Calculated values of magnetic susceptibility, $\chi$, Weiss constant, $\theta$, and exchange integral, $j$, in (0.8-x)MoO$_3$-0.2B$_2$O$_3$-xK$_2$O (0 \leq x \leq 0.25) glasses at 300 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic susceptibility $\chi$ (x10$^5$ emu/gG)</th>
<th>Weiss constant, $\theta$ (K)</th>
<th>Exchange integral, $j$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.087</td>
<td>-69.7</td>
<td>-0.012</td>
</tr>
<tr>
<td>S2</td>
<td>0.071</td>
<td>-17.4</td>
<td>-0.012</td>
</tr>
<tr>
<td>S3</td>
<td>0.61</td>
<td>-265.9</td>
<td>-0.046</td>
</tr>
<tr>
<td>S4</td>
<td>0.032</td>
<td>-334.4</td>
<td>-0.058</td>
</tr>
<tr>
<td>S5</td>
<td>0.654</td>
<td>-269.3</td>
<td>-0.046</td>
</tr>
<tr>
<td>S6</td>
<td>0.111</td>
<td>-109.0</td>
<td>-0.019</td>
</tr>
</tbody>
</table>
EPR lineshape simulation\(^2\) of the axially symmetric lineshape of S1 shows that the paramagnetic site exists as molybdenyl, MoO\(^{3+}\) ion. The table further shows that the value of the g-matrix is higher in S1, as compared with those of S2-S6, at 300 and 77 K. This is due to the fact that the addition of K\(_2\)O in S2-S6 modifies the network of S2-S6 with significant variations in the values of g-matrices with respect to S1. Also, due to the difference in structural network among S1 and S2-S6, a similar trend is observed in the values of A-interaction matrices in S2-S6 at 300 and 77 K. The values of g-matrices in these glasses at 77 K are slightly less than those at 300 K (Table 3). This result may be attributed to the overall crystal field effect in the network due to variation of temperature from 300 – 77 K. Unlike the cases of g- and A-interaction matrices, the derivative EPR peak-to-peak linewidth (\(\Delta H\)) do not show any significant variation in the glasses S1-S6, at 300 and 77 K and also between the values at the above two temperatures. This result shows that the Mo\(^{5+}\)(4\(d^1\)) small polaron hopping rate is not affected significantly in the temperature range 300–77 K.

### Conclusions

The above studies shows the presence of octahedral [OMoO\(_{5/2}\)], tetrahedral [BO\(_{4/2}\)] and trigonal [BO\(_{n-3/2}\)]\(^n\) units \(n = 1, 2, 3\) contains trigonal [BO\(_{n+(3-n)/2}\)]\(^n\) \(n = 1,2,3\) units a 300 K. The Mo\(^{5+}\)(4\(d^1\)) ion concentrations are one order of magnitude lower than those of Mo\(^{6+}\) ions. The calculated values of the magnetic susceptibilities \(-10^{-5}\) emu/gG indicate the weak paramagnetism in the glasses at 300 K. The EPR results show that the lineshape varies from axially symmetric (S1) to isotropic in S2-S6, at 300 and 77 K. The negative g-shift indicates that the Mo\(^{5+}\)(4\(d^1\)) is the paramagnetic site in the glasses which exists as molybdenyl, MoO\(^{3+}\), ion. The partially resolved hyperfine structures in S2-S6 indicate small polaron hopping in the matrix which depends on temperature as well as on the glassy network. The values of the exchange integrals in the range 0.003-0.058 eV (\(\sim 10^{11}-10^{12}\) Hz) indicate phonon assisted hopping of the Mo\(^{5+}\)(4\(d^1\)) small polaron in the glassy matrices.

### Table 3—Observed values of g- and A-matrices and derivative EPR peak-to-peak linewidth (\(\Delta H\)) of the (0.8-x)MoO\(_3\)-0.2B\(_2\)O\(_3\)-xK\(_2\)O \((0 \leq x \leq 0.25)\) glasses at 300 and 77 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>(g)-matrix</th>
<th>A-matrix (\times 10^4) cm(^{-1})</th>
<th>Peak-to-peak linewidth, (\Delta H) (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 K</td>
<td>77 K</td>
<td>300 K</td>
</tr>
<tr>
<td>S1</td>
<td>(g_\parallel = 1.940)</td>
<td>(g_\parallel = 1.935)</td>
<td>(A_\parallel = 150.0)</td>
</tr>
<tr>
<td></td>
<td>(g_\perp = 1.974)</td>
<td>(g_\perp = 1.975)</td>
<td>(A_\perp = 35.6)</td>
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<tr>
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<td>(g_{iso} = 1.963)</td>
<td>(g_{iso} = 1.962)</td>
<td>(A_{iso} = 73.7)</td>
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<td>S2</td>
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<td>45.9</td>
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References