Influence of MoO$_3$ on the Structure of Lithium Aluminum Phosphate Glasses

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IR spectroscopy, density and ultrasonic velocity measurements have been carried out for aluminum lithium phosphate glasses with and without MoO$_3$. The observed changes in the FTIR spectra of the glasses were related to the modifier/former role of molybdenum ions. The results revealed that the density increases with increasing MoO$_3$ content, which was attributed to the increase in the compactness and packing of the glass network. The ultrasonic data were analyzed in terms of creation of new bonds of MoO$_3$ attached to phosphate units. The new bonds increased the average crosslink density and the number of network bonds per unit volume along with a strengthening of the different modes of vibrations which in its turn increased the ultrasonic velocity, the rigidity and hence the elastic moduli of the glasses.

Keywords: phosphate glasses, IR, density, elastic properties.

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1. Introduction

Lithium phosphate glasses have been gained great attention during the last decades due to their wide range of compositional and structural possibilities. The low melting and glass transition temperatures, high electrical conductivity, high thermal expansion coefficient of these glasses enable their use in laser host matrices, lithium micro-batteries or in electro-optical systems (CHOWDARI, 1988; SELVARAJ, 1988; CHOWDARI, 1991; DONALD, 1993; Proulx, 1994; JIANG, 1998; HUDGENS, 1998; BROW, 2000; CAMPBELL, 2000; DAI, 2002; Sharaf El-Deen, 2008; COZAR et al., 2008). The physical properties of phosphate glasses can be improved by introducing alumina, which provides higher chemical durability, alkali and transition metal oxides like MoO$_3$ (BRIDGE et al., 1986; 1987; CHEN, 1999; REIS et al., 2002).

It was reported that the network of lithium phosphate glasses is a polymeric arrangement of phosphate groups with variable lengths, and is dominated by linkages between PO$_4$ tetrahedra. Addition of Li$_2$O to P$_2$O$_5$ converts the three-dimensional phosphate network into linear phosphate chains, and changes the phosphate structural groups from PO$_4$ to PO$_3$ to PO$_2$ to PO as the molar ratio of Li$_2$O/P$_2$O$_5$ passes from 0 to 1, to 2 and to 3. The linear chain structure results in a cleavage of P-O-P linkages and a creation of non-bridging oxygens (NBO’s) in the glass (WELLS, 1975; RAO, 2002; PRASAD, 2005; ELBATAL et al., 2008; SUBČIK et al., 2009). On the other hand, the structure of MoO$_3$-P$_2$O$_5$ glasses were stated to belong to a group of glasses, which incorporate distorted octahedral structural units [MoO$_6$] or tetrahedral structural units [MoO$_4$] within the glass network. MoO$_3$ plays a modifier role upon the addition of MoO$_3$ to P$_2$O$_5$ glasses with ratio <50 mol% by forming non-bridging oxygens, and a former role when MoO$_3$ > 50 mol% throughout the complete Mo-P-O range by increasing the crosslink density of P$_2$O$_5$ (BRIDGE et al., 1986; 1987; MOUSTAFA et al., 1998).

Introducing molybdenum ions in lithium phosphate glasses produces some variable interesting electrical properties which are related to the ability of molybdenum ions to exist in glasses in three possible valences, namely Mo$^{3+}$, Mo$^{5+}$ and Mo$^{6+}$ (BH et al., 2008; ELBATAL et al., 2008; CHOWDARI et al., 1991). Recently, it was found that substitution of PbO by MoO$_3$ in MoO$_3$–PbO-La$_2$O$_3$–P$_2$O$_5$ glasses leads to a polymerization of the phosphate chains by increasing the packing and the cross link density of the phosphate network (SADDEEK, 2011). Accordingly, this work aims...
to extend the available informations of MoO$_3$ in the environment of the Al$_2$O$_3$-P$_2$O$_5$-Li$_2$O glass system by using FTIR and ultrasons to study its availability for the use in opto-electronic devices in a further work.

2. Experimental procedures

Glass samples with the formula $x$ MoO$_3$-2Al$_2$O$_3$-68P$_2$O$_5$-30Li$_2$O with 0 $\leq x \leq 40$ wt% were prepared by the melt-quenching technique. The starting materials to obtain these glasses are (NH$_4$)$_2$HPO$_4$, Li$_2$O, Al$_2$O$_3$ and MoO$_3$ of reagent grade purity. The starting materials were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixture was melted in a porcelain crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of about 1273 K for 2 h to homogenize the melt. The obtained glass samples from the melt quenching into preheated stainless-steel mould were heat treated at a temperature of about 20 K below their calorimetric glass transition temperature for 2 h to remove any internal stresses. The obtained glasses were lapped and two opposite sides were polished to be suitable for use in the ultrasonic velocity measurements. Non-parallelism of the two opposite side faces was less than 0.01°. The composition given in table 1 refers to the nominal composition (the starting mixture). The glass samples were kept in desiccators to prevent possible attack by moisture. X-ray diffraction patterns were recorded to check the amorphous nature of the glass samples using a Philips X-ray diffractometer PW/1710 with Ni-filtered Cu-K$_\alpha$ radiation ($\lambda = 1.542 \, \text{Å}$) powered at 40 kV and 30 mA. The patterns (not shown) revealed broad humps characteristic of the amorphous materials and did not reveal discrete or any sharp peaks.

Infrared (IR) spectra for the glass powder (after crushing them into powder form) were obtained using an IR Fourier spectrophotometer type JASCO, FT/IR–430 (Japan). For this purpose, each sample was mixed with KBr in the proportion of 1 : 100 (by weight) for 20 min and pressed into a pellet using a hand press. At least two spectra for each sample were recorded in the wavenumber range of 400–2000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$, corrected for dark-current noise and normalized. The resulted spectra were curving fitted (PRÔULX et al., 1994) to get quantitative values for the band areas of heavily overlapped bands. The curve-fitting procedure is based on a least-squares minimization which in its turn involves entering the values of the wavenumber of the component bands (determined by using the deconvolution technique) and then a program determines the best estimate of the parameters of the component curves. The deconvolution process involves several steps: computation of an interferogram of the sample by computing the inverse Fourier-transform of the spectrum, multiplication of the interferogram by a smoothing function and by a function consisting of a Gaussian–Lorentzian band shape and Fourier transformation of the modified interferogram. The deconvolution procedure is typically repeated iteratively for best results. At iteration, the line shape is adjusted in an attempt to provide narrower bands without excessive distortion. Therefore, each IR spectrum has its characteristic peak positions.

The density $\rho$ of the glass samples was determined using the Archimedes technique by applying toluene as an immersion fluid. At least, three samples of each glass were used to determine the density. A random error in the density values was found as ±1%. The molar volume $V_m$ has been determined as $M/D$, where $M$ is the molar weight of the glass. The values of the packing density ($V_t$) were calculated as $V_t = (1/V_m) \sum V_i x_i$, where $V_i = (4\pi/3)N_A[mR^3_A + nR^3_O]$, $R_A$ and $R_O$ are the Pauling radii (Å) of ions in the oxide $A_mO_n$.

The ultrasonic velocities, longitudinal ($v_L$) and shear ones ($v_T$), at room temperature (∼300 K) were obtained using the pulse-echo method. In this method, x-cut and y-cut transducers (KARL DEUTSCH) operated at the fundamental frequency of 4 MHz along with a digital ultrasonic flaw detector (KARL DEUTSCH Echograph model 1085) were used. The uncertainty in the measurement of the ultrasonic velocity is ±10 m/s. Besides the density, two velocities were utilized to determine two independent second-order elastic constants (SOECs): $C_{11}$ and $C_{44}$. For the pure longitudinal waves $C_{11} = \rho v^2_L$, and for the pure transverse ones $C_{44} = \rho v^2_T$. The bulk modulus ($K_e$), Young’s modulus ($Y$), the Debye temperature ($\theta_D$) and the Poisson’s ratio ($\sigma$) may be determined using the standard relations (RAO, 2002):

$$\sigma = 1/2 - C_{44}/2(C_{11} - C_{44}),$$

$$Y = 2(1 + \sigma)C_{44},$$

$$K_e = C_{11} - 4/3C_{44},$$

$$\theta_D = (h/k)v_D \left[ \frac{3\eta \rho N_A}{4\pi M} \right]^{1/3},$$

where $v_D$ is the mean ultrasonic velocity given by

$$\left[ \frac{1}{3} \left( \frac{1}{v^2_L} + \frac{2}{v^2_T} \right) \right]^{-1/3},$$

$h$ is the Planck’s constant, $N_A$ is the Avogadro’s number, and $k$ is the Boltzmann’s constant. The uncertainty in the measurement of the elastic moduli is ±0.15 GPa.

3. Results and discussion

3.1. Structural analysis

Figure 1 shows the IR spectra of the Al$_2$O–Li$_2$O-P$_2$O$_5$ glass system with and without MoO$_3$. Figures 2 a–c show the deconvolution of the IR spectrum of the glasses containing different ratios of MoO$_3$ wt% as an
example. The main features of the IR spectra of the studied glasses are four bands at \(\sim 525\), \(\sim 745\), \(\sim 1088\) and \(\sim 1645\) cm\(^{-1}\). The presence of MoO\(_3\) creates two additional bands at \(\sim 1268\) and \(\sim 1430\) cm\(^{-1}\). The common IR features of these glasses are that the absorption bands for glasses containing MoO\(_3\) become wider, and their broadening increases with the increasing MoO\(_3\) content. Moreover, the absorption bands are strongly overlapped especially at \(\sim 525\) and \(\sim 1000\) cm\(^{-1}\). The position of the absorption band at \(\sim 745\) cm\(^{-1}\) was shifted to a lower wavenumber and its area became decreased. Moreover, the absorption band at 1000 cm\(^{-1}\) was shifted to a higher wavenumber.

![Fig. 1. Infrared absorption spectra of the glass system 2Al\(_2\)O\(_3\)-30Li\(_2\)O-68P\(_2\)O\(_5\)-xMoO\(_3\) (0 \(\leq\) x \(\leq\) 40 wt%).](image)

The IR absorption at around 520 cm\(^{-1}\) is attributed to the bending vibrations of the O=PO linkages (Ciceo Lucacel et al., 2009). This band may be superimposed with the vibrations of the MoO\(_6\) structural units that play a modifier role (Little Flower et al., 2007). The bands at around 745 cm\(^{-1}\) are assigned to asymmetric stretching vibrations of the P–O–P rings (Mostafa et al., 1998). The bands at around 910 cm\(^{-1}\) are related to P–O–P symmetric stretching vibrations of bridging oxygen atoms in the P–O–P bonds (Sudarsan et al., 2004). The band at around 995 cm\(^{-1}\) can be ascribed to symmetric stretching vibration of the PO\(_4\)\(^{3-}\) tetrahedra (P–O\(^{-}\) ionic group) (Jastrzebski et al., 2011; Lazarev, 1968; Ciceo Lucacel et al., 2009). This band may be overlapped with another one ascribed to the Mo-O stretching vibration in the [MoO\(_4\)]\(^{2-}\) units that play a former role (Subčík et al., 2009). The vibrational bands at around 1275 and 1410 cm\(^{-1}\) have been attributed to the asymmetric stretching of the double bonded oxygen vibrations and to the symmetric stretching mode of P=O (Sudarsan, 2004; Magdas et al., 2008). In addition to the above features, there is a small absorption band in the spectra of all glasses at around 1660 cm\(^{-1}\). Such a band

![Fig. 2. Band deconvolution of the IR spectrum for 2Al\(_2\)O\(_3\)-30Li\(_2\)O-68P\(_2\)O\(_5\)-xMoO\(_3\) glass (0 \(\leq\) x \(\leq\) 40 wt%; a) x = 10, b) x = 20, c) x = 30](image)
was attributed to the bending vibrations of O-H bonds brought by air moisture during the preparation of the KBr pellets for the infrared measurements (Khafagy, 2001; Boudlich et al., 2002).

Recently, it was reported that in Li$_2$O-P$_2$O$_5$ glasses, the increase of the Li$_2$O content causes the formation of terminal phosphate groups PO$_2^-$ and an increase in the average length of the P=O bond (Ivascu et al., 2011). An addition of Al$_2$O$_3$ to lithium phosphate glasses causes a shift of the main absorption bands of the PO$_4$ units to higher wavenumbers. This shift was attributed to two reasons; the first one is the formation of P-O-Al bridging bonds connected to phosphate groups instead of P-O-Li bonds where Al-O has a higher bond strength than P-O; the second one is the formation of charge compensation pairs between Li$^+$ and the aluminum (VI) polyhedra (Brow, 2000; Manupriya, 2009; LiDE, 2004). Therefore, as represented in the studied glass system, as the MoO$_3$ content is increased, for $0 \leq x \leq 20$ and $20 \leq x \leq 40$ (wt%) two regions can be formed in the IR spectra as shown in Fig. 1. The features of the first region are:

a) The intensity of the vibrational bands related to the phosphate glasses is decreased,

b) The bands due to symmetric stretching vibrations of P-O-P rings are shifted to a lower wavenumber,

c) The bands due to P-O-P asymmetric stretching vibrations of the bridging oxygen atoms in the P-O-P bonds are rapidly shifted to a higher wavenumber.

These features suggest the modifier role of MoO$_3$ by breaking up the P-O-P linkages and occupying the positions between P-O-P layers creating NBOs to form MoO$_6$ without a change of the number of P=O bonds the features of the second regions are:

a) The intensity of the illustrated vibrational bands related to the phosphate glasses is increased,

b) The whole of the latter bands are shifted to a higher wavenumber.

The shift of the bands can be explained by taking into account the strength of the bands and the effect of the bond energy of Mo-O. The strength of the vibrational bands can be attributed to the decrease in the phosphate chains length, the increasing ratio of the oxygen atoms to the phosphorus ones (O/P), and to the bridging of Mo with oxygen atoms to form [MoO$_4$]$_2^{2-}$ units which have a former role. In this region, MoO$_3$ enters the glass network by breaking up the P-O-P linkages and forming P-O-Mo bonds. Accordingly, the P=O bond will be converted into bridging oxygen and the phosphate bonds will be shortened (Higazy, 1985; Cozar et al., 2006). The overlapping of the absorption bands in this region confirmed the formation of shorter bonds, and the value of O/P larger than 3 confirmed the rupture of P=O bonds. A similar behavior in tungsten lead phosphate glasses has been observed (Abid et al., 2002).

### 3.2. Analysis of the elastic moduli

Table 1 shows the values of the density of MoO$_3$-Li$_2$O-Al$_2$O$_3$-P$_2$O$_5$ glasses with the different additions of MoO$_3$. The values of the density of the studied glasses agree well with that reported elsewhere (Abid, 2002; Montenero, 2004; Cozar et al., 2006). In general, both the packing of the glass network and the molecular weight of each contributed oxide affect the density in the glass system. It is generally accepted that the density increases when the concentration of the third component (MoO$_3$) is increased while the ratio of the other concentrations remain always constant.

On the other hand, the packing density of Li$_2$O, Al$_2$O$_3$, P$_2$O$_5$ and MoO$_3$ are considered to be 8, 21.5, 34.8 and 21.3 m$^3$mol$^{-1}$, respectively (Wells, 1975; Saddeek, 2011). Accordingly, the Mo$^{3+}$ ions can occupy an interstitial position in the interstices of the lithium phosphate network increasing the connectivity of the structure with further addition of the MoO$_3$ content. Thus, the increase in the density can be related to the constitution of the glasses rather than to the type of the structural unit.

As reported earlier, the ultrasonic velocity into a glassy material depends on the rigidity, cross-link density and the number of bonds per unit volume of the structure of the glasses, i.e. a harder material will produce a higher velocity, whereas a softer material will produce lower velocity, irrespective of their densities (Bridge, 1986; Saddeek, 2007; Eraiah et al., 2010). The variation of the values of the longitudinal and shear ultrasonic wave velocities with the MoO$_3$ content is listed in Table 1. The ultrasonic velocities, Debye temperature ($\theta_D$), and the elastic moduli, i.e. the Young’s modulus (Y) and bulk modulus (K$_b$) of the studied glasses, increase while the Poisson’s ratio decreases with the increase of the MoO$_3$ content.

According to the IR analysis, there is some type of modification of the chemical bonds linked to the phosphate structural units with the addition of MoO$_3$ in the interstices of the lithium phosphate network. This addition creates [MoO$_4$]$_2^{2-}$ structural units bridging oxygens and smaller rings of the phosphate groups. This creation is associated with an increase of O/P and bridging bonds P-O-Mo that has high bond energy. These factors contribute to the increase of the average crosslink density ($n_c$) and to the number of network bonds per unit volume ($n_b$) of the glass system. The average crosslink density and the number of network bonds per unit volume can be estimated according to an earlier work (Higazy et al., 1985). Thus, the observed increase in the ultrasonic velocity can be explained by assuming that, Mo$^{3+}$ enter interstitially and as a result some type of modification of the P-O-P, and Li-O-P linkages, which already exist in the glass, into Mo-O-P, and Li-O-P bonds will occur. The conversion of these linkages results in an increase in
the packing density, which contract the glass network. Therefore, the structure of the glass will be strengthened and hence the increase of the rigidity will contribute to the increase in the ultrasonic velocity.

In solid materials, the Debye temperature ($\theta_D$) plays an important role in the determination of elastic moduli and atomic vibrations. $\theta_D$ represents the temperature at which all the low frequency ‘lattice’ vibrational modes are excited (RAO, 2002). As a consequence, the Debye temperature, $\theta_D$, which depends directly on the mean ultrasonic velocity and on the atomic vibrations of the lighter structural groups like phosphates will increase as the MoO$_3$ content increases. The increase in $\theta_D$ can be explained by taking into account two factors. Firstly, the clear shift of the vibrational modes in the IR absorption spectra towards higher frequencies as the MoO$_3$ content increases and the change in the relative strength of bonds in the glass network. The bond strength of Li$_2$O, Al$_2$O$_3$, P$_2$O$_5$ and MoO$_3$ are 77.9, 119.2, 28.2 and 69.8 $\times$ 10$^9$ J m$^{-3}$ (LIDE, 2004). The increase of the bond strength, the rigidity and the average cross-link density of the studied glasses decrease the Poisson’s ratio.

The values of the bulk modulus ($K_v$) and Young’s modulus ($Y$) are listed in Table 1. As discussed before, addition of MoO$_3$ to the Li$_2$O-Al$_2$O$_3$-P$_2$O$_5$ glass creates new linkages attached to the phosphate structural units. These linkages have a high bond energy and increase both the number of bonds per unit glass formula unit and the packing density of the glass structure. On the other hand, the bulk modulus of a covalent network is determined by the bond density (number of bonds in a unit volume), and by the stretching force constant. The stretching force constant is related to the cation field strength of the modifier, i.e. high field strength cations polarize their environment strongly and enhance the ion-dipole interaction. Thus, the increase in the packing density can be attributed to two factors, firstly, the change in the coordination polyhedra of MoO$_3$ from MoO$_6$ to MoO$_4$, which in its turn change the type of bonding of the investigated glasses and secondly, the local contraction of the network around the Mo and Li cations that have a high-field-strength which polarizes their environment strongly and enhances the ion-dipole interactions. However, the elastic moduli are sensitive in a greater extent to the density of covalent bonds in the structure, which resist deformation. Therefore, it can be concluded that the elastic moduli will increase and these conclusions are in agreement with that reported earlier (DAMODARAN, 1989; SIDKEY, 2002; MUÑOZ et al., 2004; SADDEEK et al., 2009).

### Table 1. The density ($\rho$), packing density ($V_t$), longitudinal ($v_l$) and shear ($v_T$) ultrasonic velocities, Debye temperature ($\theta_D$), Poisson’s ratio ($\sigma$), average cross link density ($n_b$), number of network bonds per unit formula unit ($n_x$), Young’s modulus ($Y$), and the bulk modulus ($K_v$) of the glass system 2Al$_2$O$_3$-30Li$_2$O-68P$_2$O$_5$-xMoO$_3$ glass (where $x = 0, 10, 20, 30$ and $40$ wt.%).

<table>
<thead>
<tr>
<th>Composition of glass wt%</th>
<th>$\rho$ [kg/m$^3$]</th>
<th>$V_t$ [m/s]</th>
<th>$v_l$ [m/s]</th>
<th>$v_T$ [m/s]</th>
<th>$\theta_D$ [K]</th>
<th>$\sigma$</th>
<th>$n_b$ × 10$^{28}$</th>
<th>$Y$ [GPa]</th>
<th>$K_v$ [GPa]</th>
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<tr>
<td>Li$_2$O</td>
<td>Al$_2$O$_3$</td>
<td>P$_2$O$_5$</td>
<td>MoO$_3$</td>
<td>30</td>
<td>2</td>
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<td>3758</td>
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</table>

4. Conclusion

The analysis of IR spectra indicates that the Mo$^{3+}$ ions are preferentially incorporated into the phosphate network as former forming the [MoO$_4$]$^{2-}$ units. New bonds have a high bond strength and bridging oxygens were created. The sound velocities, Debye temperature, and the elastic properties show an increasing trend with the increase in the MoO$_3$ content. This behavior was attributed to the increase of the cross link density; the number of network bonds per unit volume, the rigidity as well as the high-field-strength of Mo$^{3+}$ polarizes their environment strongly.

Further work is required to study the electrical and optical properties of these materials with and without the radiation effect to improve the use in opto-electronic devices.

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