FTIR Spectra and Optical Properties of Molybdenum Phosphate Glasses

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ABSTRACT

Glasses in the system 5Na₂O-5ZnO-5Al₂O₃-65P₂O₅-xMoO₃-(20-x)CaO, mol%; where x = 0, 2, 5, 7, 10, 12, 15, 20, have been prepared using the conventional melting and annealing method. Density and molar volume of these glasses were measured. Density was found to increase monotonically with increasing $x$ (i.e. molybdenum oxide content) and, conversely, the molar volume decreased with increasing $x$. UV-visible optical absorption spectra of the prepared glasses were measured from 190 to 1100 nm. These spectra exhibit charge transfer bands due to iron trace impurities which eventually affect the induced absorption due to MoO₃ and that due to the host base glass in the UV-region. The UV-absorption edge, both direct and indirect allowed transitions with their optical energy gaps, has been studied. Also, the Urbach energy was evaluated. The refractive index and the extinction coefficient data were used to evaluate the absorption coefficient of the different glass compositions. The molar refraction, electronic polarizability and the optical basicity were obtained using the evaluated glass refractive indices. Fourier transform infrared (FTIR) spectra of the investigated glasses have been studied in order to understand the characteristic frequencies of the vibrational chemical bonds which are liable to the structural and spectral changes. These spectra showed IR absorption bands related to the characteristic phosphate and molybdate bonds especially P=O, P—O—P, O—P—O, P—O—H, P—O—Mo and Mo—O—Mo.

Key words: Molybdenum phosphate glass; Optical properties; FTIR

Introduction

Phosphate glasses have been selected for this study mainly for four reasons: (a) phosphate glasses are usually low melting, (b) phosphate glasses are believed to be highly acidic and hence can produce a reasonable concentration of the reduced state of the transition metal ions even on ordinary melting in air. (c) phosphate glasses are potentially good UV-transmitting materials and (d) phosphate glasses offer an important range of compositional possibilities with which it is possible to tailor physical and chemical properties of interest for specific technological applications.

Stevels et al., (1947) early suggested that the intrinsic absorption edge of an oxide glass corresponding to the transition of a valence electron of an oxygen ion to valence excited state, and the introduction of a modifier oxide cause a shift of the UV-edge to longer wavelengths. Later, some authors (Scholze et al., 1959; Hensler et al. 1969; Sigel et al. 1971; Kordes et al. 1968) concluded that the location of the UV absorption edge is more complex and can be related to structural rearrangement with composition. However, (Sigel et al. 1974; Sigel et al. 1977) and Pauli, (1990) have shown that UV absorption results can be partly related to the presence of impurities and specifically to the transition metal ions. (Duffy et al., 1990; Duffy et al., 1997) assumed that the ultraviolet absorption in glass arises from electronic transitions associated with the oxide species and can be regarded in terms of its state of polarization affecting the imaginary part of the refractive index, Duffy et al., (1990). Since the state of polarization depends on the basicity of the glass, there is a close connection between glass composition and ultraviolet transparency.
Phosphate glasses possess high thermal expansion coefficients, low glass transition and softening temperatures, and good optical properties, in addition to their low melting temperatures, Guo et al., (1998). The addition of molybdenum to glasses induces some interesting electronic and optical changes (Patel et al., 1983; Selvaraj et al., 1985; Gohar, 1993; Jamnicky et al., 1995; El Batal et al., 2004; El Batal et al., 2007). Some of these changes are due to the ability of molybdenum to exhibit multi-valence states (Mo$^{3+}$, Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$). Earlier studies (Weyl et al., 1959; Veinberg et al., 1962) postulated that the changes in color in Mo-containing glasses were attributable to different equilibrium between the four valence states. (Parke and Watson, 1969) studied the absorption and fluorescence spectra of molybdenum in several glasses and assumed that, in silicate and borate glasses, only pentavalent molybdenum (Mo$^{5+}$) was present. But, in phosphate glasses, trivalent molybdenum (Mo$^{3+}$) could be stabilized. Recent contributions from our laboratory have confirmed that molybdenum exists mainly in the pentavalent state in sodium borate glasses El Batal, (2004) while Mo$^{3+}$ ions are the predominant species in sodium meta-phosphate glasses El Batal, (2007).

The aim of the present work is to study the possible sites and valency states of molybdenum in phosphate glasses by optical UV-VIS, IR and optical parameters.

2. Experimental:

2.1. Glass Preparation:

Glass samples having the chemical compositions 5Na$_2$O-5ZnO-5Al$_2$O$_3$-65P$_2$O$_5$-(20-$x$)CaO, mol%; where $x = 0, 2, 5, 7, 10, 12, 15, 20$, have been prepared using the conventional melting and annealing method. The starting materials used in the present study were powders of chemically pure NH$_4$H$_2$PO$_4$, Al$_2$O$_3$, ZnO, CaCO$_3$, Na$_2$CO$_3$ and MoO$_3$. Well mixed powders containing appropriate amounts of the raw materials were melted in a porcelain crucible in an electric furnace at 1250 ºC for 1 h at normal atmospheric conditions. The glass formed by quenching the melt on a preheated stainless-steel mold was immediately transferred to another muffle furnace where it was annealed at about 480 ºC for 1 h. Then, the muffle was switched off and the temperature decreased to room temperature with a rate 25 ºC/h.

2.2. Density Measurement:

Density ($\rho$) of the glass samples was calculated employing Archimedes principle at room temperature using distilled water as immersion fluid and applying the following relation:

$$\rho = \rho_b \frac{W_a}{W_a - W_b}$$

where $\rho_b$ is the density of the buoyant (in case of water equals 1), $W_a$ and $W_b$ are the sample weights in air and the buoyant, respectively. At least, three samples of each glass were used to determine the density and the determined values are precise to ±0.001 g/cm$^3$. The molar volume (Vm) of glass is defined as the mean molecular weight of its constituents divided by its density ($\rho$) as given by the equation:

$$V_m = \frac{M}{\rho}$$

where $M$ is the mean molar weight of the glass expressed as the mole fractions of the oxides multiplied by their molecular weights.

2.3. Optical Measurement:

For the UV–visible spectra rectangular samples of the dimensions 1.5X0.9X0.2 cm$^3$ were ground and perfectly polished. The optical measurements of the polished glass samples (thickness 2 mm) were recorded at room temperature using a double beam spectrophotometer, with automatic computer data acquisition, (Type Jasco, V-570, Relll-00, UV-vis-NIR) at photometric accuracy of ±0.002–0.004 absorbance and ±0.3% transmittance, employed to record the optical transmission and reflection spectra of the glass samples over the wavelength range of 200–2500 nm, at normal light incidence.

KBr pellet technique was used to obtain the Fourier transform infrared (FTIR) spectra of the glasses, at room temperature. The spectra were recorded in the wavenumber range of 4000-400 cm$^{-1}$ using 100 scans at 2 cm$^{-1}$ resolution by an infrared spectrophotometer type Jasco FTIR-300E (Japan).
Results and discussion

3.1. Density and Molar Volume:

Density is a powerful tool capable of exploring the changes in the structure of glasses. Density is affected by the structural softening/compactness, change in geometrical configuration, co-ordination number, cross-link density and dimension of interstitial spaces of the glass. Thus, the addition of any transition metal ions to the glass leads to a linear variation, i.e. either increase or decrease in the density with changing composition Dowidar et al., (2009). Values of the density (ρ) and molar volume (V_m), together with the chemical composition, of the investigated molybdenum phosphate glasses are listed in Table 1. As indicated in Fig. 1, density increases monotonically with increasing molybdenum oxide content, at the expense of CaO content; and, conversely, the molar volume decreases with increasing MoO_3 content. This is an expected result as the heavy metal oxide (MoO_3) replaces the lighter oxides (CaO). In general, it is also expected that the density and the molar volume show opposite behavior to each other.

Table 1: Chemical composition, density (ρ) and molar volume (V_m) of studied glasses.

<table>
<thead>
<tr>
<th>Glass compositions</th>
<th>ρ</th>
<th>V_m</th>
</tr>
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<tbody>
<tr>
<td>MoO_3 Na_2O P_2O_5 CaO ZnO Al_2O_3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>2.2557</td>
<td>51.7593</td>
</tr>
<tr>
<td>G2</td>
<td>2.5828</td>
<td>45.3962</td>
</tr>
<tr>
<td>G3</td>
<td>2.6439</td>
<td>44.6293</td>
</tr>
<tr>
<td>G4</td>
<td>2.6589</td>
<td>44.5663</td>
</tr>
<tr>
<td>G5</td>
<td>2.707</td>
<td>44.0499</td>
</tr>
<tr>
<td>G6</td>
<td>2.7321</td>
<td>43.8277</td>
</tr>
<tr>
<td>G7</td>
<td>2.7790</td>
<td>43.357</td>
</tr>
<tr>
<td>G8</td>
<td>2.7820</td>
<td>43.1758</td>
</tr>
</tbody>
</table>

Fig. 1: Variation of the density and molar volume of the studied molybdenum phosphate glasses with changing MoO_3 content.

3.2. UV Absorption:

Fig. 2 reveals the absorption spectra extending from 200 to 1100 nm of the base undoped and Mo-doped P_2O_5–Al_2O_3–Na_2O–ZnO–CaO glasses. The spectra reveal a strong ultraviolet band extending from 200 to 350 nm with two significant peaks at 270 nm and 340 nm followed by a clear medium visible broad band centered at 430 nm for G1 sample. At very low MoO_3 content (2%), the absorption spectrum showed very strong ultraviolet absorption extending from 200 to 400 nm with two obvious peaks at 265 and 315 nm followed by a clear medium visible broad band centered at 435 nm for G2 sample. At MoO_3 contents (5, 7, 10%), the UV–VIS absorption spectra showed almost the same spectral features except for a low intense and broad visible band centered at 750 nm. With increasing MoO_3, the UV spectrum increased and showed three peaks at about 230, 285 and 340 nm, while the remaining visible absorption revealed a peak at 440 nm followed by very close spectral curves for G3, G4 and G5 samples as shown in Fig. 2. At the highest MoO_3 level (10, 12, 15, 20%), the spectrum initially showed very broad absorption extended from 200 to 400 nm revealing four peaks at 205, 235, 340 and 400 nm, followed by two extra broad visible bands centered at about 540 and 750 nm for G6, G7 and G8 samples as shown in Fig. 2.
It is evident that the studied undoped calcium phosphate glass, shows strong UV absorption, which is similar to the UV spectrum of sodium meta-phosphate glass Marzouk et al., (2006) but with different peak maxima. In 1968, (Sigel and Ginther, 1968) and later in 1982, (Cook and Mader, 1982; Natura et al., 1999) correlated the UV absorption in various commercial glasses with contamination of trace iron impurities within the raw materials used for glass preparation. Recently, (Ehrt et al., 2000; Ehrt, et al., 2002; Möncke et al., 2004; Möncke, et al., 2006) and (Marzouk et al., 2011; El Batal et al., 2008) identified and confirmed that UV absorption, observed in phosphate, silicate and other glasses, originates from trace iron impurities, even at the ppm level.

The introduction of Al₂O₃ to the studied glass causes increase in the intensity and shifts the absorption bands to longer wavelengths (Fig. 4). This can be attributed to the difference in bonding strength, which depends on the electro-negativity and ionic radius of the introduced cation Al³⁺. Also, the coordination of Al³⁺ can be 4 and/or 6; which of these two coordinations is established depends on the bonding state of O²⁻. Then, through formation of AlO₄ tetrahedron, the number of non-bridging oxygens (NBO) lower down, which increases the intensity Marzouk, et al., (2008).

Based on previous hypotheses concerning the sharing of trace iron impurities (mainly Fe³⁺) and the capacity of divalent Al³⁺ ions to produce UV absorption within closer positions, it is suggested that the UV absorption spectra experimentally observed for the studied base calcium phosphate glass are due to a combination of the absorption due to two species, namely Fe³⁺ and Al³⁺ ions. However, further studies are
Fig. 4: Determination of the optical energy band gap from \((ahv)^{1/2}\) and \(hv\) for studied glasses.

needed to clarify the specific absorption component of each species by combining techniques and utilizing extra pure materials.

The base \(P_2O_5–Al_2O_3–Na_2O–ZnO–CaO\) glass with a meta-phosphate composition is expected to favor the lower oxidation states for molybdenum ions, namely Mo\(^{3+}\), Mo\(^{4+}\) and Mo\(^{5+}\). Mo\(^{6+}\) ions are known to have no unpaired electrons and are, thus, expected to give no visible absorption Albert Cotton \textit{et al.}, (1999). The sample containing the lowest MoO\(_3\) content (2\%) exhibited wide UV absorption and a visible band at 430 nm. This specific band is related (Parke \textit{et al.}, 1969; Bingham \textit{et al.}, 1965; Baugher \textit{et al.}, 1972) to the presence of Mo\(^{3+}\) ions. The second sample with 5\% MoO\(_3\) showed wider UV absorption, including a new UV peak at 330 nm and a further new broad visible band centered at 750 nm, which may be related to Mo\(^{5+}\) ions (Baugher \textit{et al.}, 1972; El Batal, 2004). It is, therefore, suggested that trivalent molybdenum Mo\(^{3+}\) ions are the main component in the host phosphate glass. With samples containing higher concentrations of MoO\(_3\), the absorption spectra revealed, in addition to the aforementioned peaks, a broad visible band at 540 nm, which is attributed (Baugher \textit{et al.}, 1972; El Batal, 2004) to Mo\(^{4+}\) ions. It is evident that the trivalent molybdenum Mo\(^{3+}\) ions are easily detected at very low concentrations, followed by pentavalent molybdenum Mo\(^{5+}\) ions and, finally, Mo\(^{6+}\) ions, which are resolved only at higher MoO\(_3\) content.

3.3. Optical Band Gap:

The optical band gap and Urbach energy of a glass are obtained from their ultraviolet absorption edges. The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically induced transition and for the provision of information about the band structure and energy gap of both crystalline and non-crystalline materials. The absorption coefficient \(\alpha(\nu)\) near the edge of each spectrum is calculated using the relation(Fuxi \textit{et al.}, 1992; Nachimuthu \textit{et al.}, 1996).

\[
\alpha(\nu) = \frac{20303}{d} A(\nu)
\]

(1)

where \(d\) is the thickness of the sample and \(A\) is the absorbance. For amorphous materials, the optical absorption at a higher value of \(\alpha(\nu)\) (\(\geq 10^3\) cm\(^{-1}\)) above the exponential tail follows a power law given by Davis and Mott, which in the most general form is given by Davis \textit{et al.}, (1970)

\[
\alpha(\nu) = B \frac{(h\nu - E_{\text{opt}})^n}{h\nu}
\]

(2)

where \(n\) is an index that can have different values: 2, 3, 1/2 and 1/3 corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. \(B\) is a constant called band-tailing parameter, \(E_{\text{opt}}\) is the optical band gap energy and \(h\nu\) is the incident photon energy. Using Eq. (2) a plot is drawn between \((ahv)^2\), \((ahv)^3\)and \((ahv)^{1/2}\) as a function of photon energy \(h\nu\) for various investigated glasses.
as shown in Figs. 3-5. From the graph, one can obtain the optical energy band gap ($E_{opt}$) for indirect allowed, indirect forbidden and direct allowed transitions. The respective value of $E_{opt}$ is obtained by extrapolating the linear region of the curve to the $h\nu$ axis where $(\alpha h\nu)^0=0$, $(\alpha h\nu)^{1/2}=0$ and $(\alpha h\nu)^{2/3}=0$ for indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively and the values are listed in Table 2 for all the samples.

The variation of $E_{opt}$ with the concentrations of MoO$_3$ content for all the samples is listed in Table 2. Fig. 5 shows that the values of $E_{opt}$ decrease with increasing MoO$_3$ content for indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. Our results may be explained on the basis that the effect of MoO$_3$ is to increase the non-bridging oxygen, spin density and thus the density of unpaired electron in unfilled bands. Also, the band tailing is so pronounced as to result in a decrease in the forbidden energy gap.

Table 2: Optical energy gap ($E_{opt}$) for different models, absorption coefficient ($\alpha$), Urbach energy ($\Delta E$), refractive index ($n$), the molar refraction ($R_m$) and the molar electronic polarizability ($\alpha_m$).

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>$E_{opt}$ (eV)</th>
<th>$E_{opt}$ (eV)</th>
<th>$E_{opt}$ (eV)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$\Delta E$ (eV)</th>
<th>$n$</th>
<th>$R_m$ (cm$^3$ mol$^{-1}$)</th>
<th>$\alpha_m$ ($\AA^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>2.7404</td>
<td>3.269</td>
<td>3.31683</td>
<td>0.000503</td>
<td>0.382</td>
<td>1.90213</td>
<td>16.30148</td>
<td>6.416914</td>
</tr>
<tr>
<td>G2</td>
<td>2.624303</td>
<td>3.2553</td>
<td>3.294</td>
<td>0.004141</td>
<td>0.4393</td>
<td>1.8701</td>
<td>16.97408</td>
<td>6.681678</td>
</tr>
<tr>
<td>G3</td>
<td>2.50875</td>
<td>3.24903</td>
<td>3.2994</td>
<td>0.00141</td>
<td>0.494345</td>
<td>1.8292</td>
<td>17.49533</td>
<td>6.886861</td>
</tr>
<tr>
<td>G4</td>
<td>2.310625</td>
<td>3.1163</td>
<td>3.2284</td>
<td>0.016893</td>
<td>0.60798</td>
<td>1.80464</td>
<td>18.16552</td>
<td>7.150675</td>
</tr>
<tr>
<td>G5</td>
<td>2.12</td>
<td>2.9029</td>
<td>3.0331</td>
<td>0.009224</td>
<td>0.81918</td>
<td>1.76331</td>
<td>18.72644</td>
<td>7.371476</td>
</tr>
<tr>
<td>G6</td>
<td>2.0319</td>
<td>2.81058</td>
<td>2.95</td>
<td>0.13555</td>
<td>0.858994</td>
<td>1.73175</td>
<td>18.91324</td>
<td>7.445006</td>
</tr>
<tr>
<td>G7</td>
<td>1.9694</td>
<td>2.7183</td>
<td>2.854</td>
<td>0.153125</td>
<td>0.8617</td>
<td>1.71566</td>
<td>20.15715</td>
<td>7.934661</td>
</tr>
<tr>
<td>G8</td>
<td>1.801</td>
<td>2.6995</td>
<td>2.8</td>
<td>0.172334</td>
<td>0.8367</td>
<td>1.68538</td>
<td>23.92834</td>
<td>9.419153</td>
</tr>
</tbody>
</table>

Fig. 5: Determination of the optical energy band gap from $(\alpha h\nu)^{0.5}$ and $h\nu$ for studied glasses.

In many crystalline and non-crystalline semiconductors, the absorption coefficient $\alpha(\nu)$ depends exponentially on the photon energy ($h\nu$). The exponential dependence known as the Urbach rule Urbach, (1953) may be written in the form:

$$\alpha(\nu) = B \exp\left(\frac{h\nu}{\Delta E}\right)$$

where $B$ is a constant and $\Delta E$ is the width of the band tails of the localized states. Plots were also drawn between ln($\alpha$) and $h\nu$, as shown in Fig. 6, and from these plots the value of the Urbach energy $\Delta E$ can be calculated from the reciprocal of the slope of the linear region of such plots and listed in Table 2. It is also interesting to observe that the Urbach energy increases with increasing MoO$_3$% content as shown in Fig. 7. (Tauc and Zanini, 1977) have suggested that the densities of states in the band tails arising from electronic transitions between localized states are exponentially dependent on energy. (Dow and Redfield, 1972) suggested that the tailing may arise from random fluctuations of the internal disorder in many amorphous solids. The Urbach energy is usually interpreted as the width of the localized states in the band gap. The origin for this tailing can be attributed to phonon-assisted indirect electronic transitions Sreekanth Chakradhar, et al., (2005)
3.4. Determination of Optical Constants:

The refractive index is one of the fundamental properties of a material. It is closely related to the electronic polarizability of ions and the local field inside the material. The refractive indices of optical material are important for applications to integrated optics devices such as switches, filters and modulators, etc. Thus, the refractive index of a material is the key parameter for device design (Neumann et al., 1979; Abdel-Baki et al., 2006). To find a solution of the inverse problem, \((R, T)\)\(\rightarrow\)\((n, k)\), which consists of calculating optical constants \(n\) and \(k\) from the overall reflectance \(R(\lambda)\) and transmittance \(T(\lambda)\) of the glass slab Fig. 7, let us first consider Fig. 8. The real part \((n)\) of the complex refractive index \((n - ik)\) of the glass is given by Khashan et al., (2000).
Fig. 8: Extinction coefficients of the glasses against wavelength.

\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \]  \hspace{1cm} (4)

where the appropriate root of the equation is considered as the refractive index. The extinction coefficient is determined by:

\[ k = \frac{\alpha \lambda}{4\pi} \]  \hspace{1cm} (5)

where \( \alpha \) is the absorption coefficient of the material and \( \lambda \) is the wavelength. According to Lambert’s absorption law, the absorption coefficient as a function of attenuation factor, \( \eta \), and the thickness of the glass sample, \( d \), is defined as:

\[ \eta(\lambda) = \exp[-\alpha(\lambda)d] \]

Thus, determination of the attenuation factor, \( \eta \), is an essential point to find the values of the optical constants of the studied materials. A method of data reduction based on an iteration technique (Khashan et al., 2000) is used in the present study to calculate the optical constants \( n \) and \( k \) from the overall reflectance \( R(\lambda) \) and transmittance \( T(\lambda) \) of the studied glass slabs. Figs. 8 and 9 represent the calculated refractive index and extinction coefficient versus wavelength of the glass series. The dispersion obeys, with a good approximation, the following empirical Cauchy dispersion equation:

\[ \frac{1}{\lambda^2} = \frac{A}{\lambda^2} + \frac{B}{\lambda^4} + \frac{C}{\lambda^6} \]

where \( A \), \( B \), and \( C \) are known as Cauchy coefficients which characterize the material. However, in the transparency region of the material, the \( C \) coefficient is very small and it can be ignored. The coefficients have the following physical significance:

\[ A = 1 + \frac{Ne^2 \lambda^2}{8\pi^2 \varepsilon_0 mc^2} \]
\[ B = \frac{Ne^2 \lambda^4}{8\pi^2 \varepsilon_0 mc^2} \]

where \( N \) determines the population of the ground level, \( e \) the charge, \( m \) the mass of the electron and \( \varepsilon_0 \) permittivity of free space. Fig. 9 demonstrates the variation of refractive index versus wavelength of the different measured glass samples. It can be seen that, the incorporation of MoO₃ notably increases the refractive index of glass. The observed increase in the refractive index and molar volume of the studied glasses...
accompanying to the addition of MoO$_3$ can be considered as an indication of an increase in number of the non-bridging oxygen associated with a structure contraction. Glasses containing polarizable entities have a potential scientific and technological importance for their non-linear optical property (Vogel et al., 1991). Within this scope, an optical investigation of phosphate glasses has been undertaken. The refractive indices measured for the different glass compositions are used to calculate the molar refraction ($R_m$), derived by (Volf et al., 1984), (Lorentz, et al., 1880). and (Wied, et al, 1880).

$$R_m = \frac{(n^2 - 1)}{(n^2 + 1)} (V_m)$$

where $n$ is the refractive index (at 587.56 nm), $V_m$ is molar volume which depending on the density and molecular weight of the glass samples, $R_m$ is known as the reflection loss. The molar refraction is related to the structure of the glass and it is proportional to the molar electronic polarizability of the material ($\alpha_m$) through the following relation:

$$\alpha_m = \frac{3}{4\pi N} R_m$$

where $N$ is the number of polarizable ions per mole, assumed to be equal to the Avogadro’s number. The values $R_m$ and $\alpha_m$ are listed in Table 2. The increase in molar refraction and increase in refractive index accompany the increase in polarizability. These findings suggest that the refractive index of the glasses depend not only on the density but also on the polarizability of the glass.

3.5. FTIR Spectra:

FTIR spectra of the studied molybdenum phosphate glasses are shown in Figs. 9 and 10. These spectra consist of two main sets of IR absorption bands in the low- and high-frequency regions. Broad bands appear in the range 3470-3445 cm$^{-1}$. These bands can be accounted for by a different role of H$_2$O molecules in the structure. In particular, the atmospheric moisture is easily absorbed by the sample or by the pellet, causing the
appearance of IR band belonging to H_2O molecules although the sample under investigation does not contain H_2O as unit in the network (Abo-Naf et al., 2004; Rafiqul Ahsan et al., 2005). The shoulders located in the range 2915-2875 cm\(^{-1}\) are relatively weak and can be ascribed to the stretching vibrations of P–O–H group in different structural sites. This group forms the strongest hydrogen bonding with the non-bridging oxygens Rafiqul Ahsan et al., (2005).

The medium band at about 1640 cm\(^{-1}\) can be attributed to the O–H bending vibration (Abo-Naf, et al., 2004). Rafiqul Ahsan, et al., 2005). The shoulder observed at 1250 cm\(^{-1}\) is assigned to the characteristic stretching mode of the P=O bond. Several previous studies (Abo-Naf et al., 2004; Rafiqul Ahsan et al., 2005; (Hafid et al., 2002); (Jermouni et al., 2003; (Metwalli et al., 2004; Doweidar et al., 2005) have shown that the band corresponding to the stretching vibration of doubly bonded oxygen could be found in the frequency range 1390-1230 cm\(^{-1}\). The asymmetric stretching vibration of O–P–O groups, \(v_s(O–P–O)\), can be found in the frequency region 1270-1200 cm\(^{-1}\), and consequently the shoulder observed at about 1200-1175 cm\(^{-1}\) can be ascribed to those groups in the present spectra. While the strong shoulder at about 1100 cm\(^{-1}\) is related to the symmetric stretching vibration of that groups, \(v_s(O–P–O)\). Previous spectroscopic study (Abid et al., 2001; (Abo-Naf et al., 2008; Jung et al., 2005) reported the asymmetric stretching vibration of the metaphosphate group, \(v_a(PO_3)\), in the range 1120–1080 cm\(^{-1}\). Therefore, in the present IR spectra, the \(v_a(PO_3)\) could interfere with the band at 1100 cm\(^{-1}\). The strong band located at about 1010-985 cm\(^{-1}\) can be attributed to the symmetric stretching vibration of the metaphosphate group, \(v_s(PO_3)\) (Abid et al., 2001; Abo-Naf et al., 2008; Jung et al., 2005). The shoulder around 895 cm\(^{-1}\) is assigned to the asymmetric stretching vibration of P–O–P linkages, \(v_a(P–O–P)\), while the relatively weak band around 745 cm\(^{-1}\) is due to the symmetric stretching vibration of that linkages, \(v_s(P–O–P)\) and/or the stretching vibration of P–O–Mo bond (El Batal et al., 2007; Abo-Naf et al., 2004; Hafid et al., 2002; Metwalli et al., 2004; Chahine et al., 2004; Jung et al., 2005). The absorption band at about 505-495 cm\(^{-1}\) may be assigned either to the harmonics of P–O–P bending vibration or to the characteristic frequency of the pyrophosphate (P_2O_7\(^{4-}\)) group (Abo-Naf et al., 2004; Abo-Naf et al., 2008).

Molybdenum ions enter the glass network former and modifier as Mo^{6+} and Mo^{5+} when linked to four or six oxygen forming MoO_4 tetrahedral and MoO_6 octahedral structural units. Previous published data (Gohar et al., 1993; El Batal, 2007; Iordanova, et al., 1994; Little Flower et al., 2007; Kashif et al., 2008; Bobkova et al., 1989; Mouhsine et al., 2003) concerning infrared spectroscopic analysis of molybdate structural units pointed out that the presence of isolated MoO_4 structural groups in the glass network can be established from
the observation of vibration bands at about 920-900, 850-830, 800 and 430-410 cm\(^{-1}\). Also, Mo–O stretching frequency of MoO\(_6\) octahedra can be found in the region 1000-940 cm\(^{-1}\). Asymmetric and symmetric vibrations of Mo–O–Mo linkages can be observed around 600 and 450 cm\(^{-1}\), respectively. In view of these observations, and taking into account the broadening character observed in such regions of the current spectra, vibration of isolated MoO\(_4\) units could interfere with the shoulder at about 895 cm\(^{-1}\), that of the Mo–O in MoO\(_6\) octahedra could also interfere under the bands in the range 1010-985 cm\(^{-1}\) and that of the Mo–O–Mo linkage under the shoulder at about 445 cm\(^{-1}\).

Conclusions:

Study of the influence of MoO\(_3\) on the optical properties of P\(_2\)O\(_5\)-Al\(_2\)O\(_3\)-Na\(_2\)O-ZnO-CaO glasses was conducted by measuring density, UV and optical parameters. In the present work, the optical constants of the glasses are determined in a wide spectral range. The measurements of glass refractive index indicate that the glass becomes optically more dispersive with a higher refractive index as the content of MoO\(_3\) increases. Analysis of absorption edges yields both direct and indirect allowed transitions with their optical energy gaps and evaluation of the Urbach energy. Therefore, the molar refraction and molar electronic polarizability are computed using the measured glass refractive indices. Infrared spectra of the investigated glasses showed IR absorption bands related to the characteristic phosphate and molybdate bonds especially P=O, Panuts-O, Oanuts-P, Panuts-O, Panuts-O, Panuts-O, Panuts-O.

References


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