Optical properties of the Na₂O–B₂O₃–Bi₂O₃–MoO₃ glasses

Yasser B. Saddeek, K.A. Aly, A. Dahshan, I.M. El Kashef

1. Introduction

The most common applications of glasses are based on their optical transparency in the visible region in a designed range of wavelengths. Application of glasses for making optical instruments and lenses is based on properties like refractive index and its dispersion, which can be varied by varying chemical composition. One of the more important applications based on optical properties of glass today is in the field of information technology through the use of glass fibers for transatlantic communication cables, telecoms and cable TV.[1]

Optical properties

The glass samples having the general chemical formula (100 − x)Na₂B₄O₇–0.5Bi₂O₃–0.5MoO₃, with 0 ≤ x ≤ 40 mol%, have been prepared using the melt quenching technique. The optical transmittance and reflectance spectrum of the glasses have been recorded in the wavelength range 300–1100 nm. The values of the optical band gap E_g for indirect transition and refractive index have been determined for 0 ≤ x ≤ 40 mol%. The average electronic polarizability of the oxide ion α_el and the optical basicity have been estimated from the calculated values of the refractive indices. The variations in the different physical parameters such as the optical band gap, the refractive index, the average electronic polarizability of the oxide ion and the optical basicity with Bi₂O₃ and MoO₃ content have been analyzed and discussed in terms of the changes in the glass structure. The results are interpreted in terms of the increase in the number of non-bridging oxygen atoms, substitution of longer bond-lengths of Bi–O, and Mo–O in place of shorter B–O bond and the change in Na⁺ ion concentration.

© 2009 Elsevier B.V. All rights reserved.
mixture was melted in a Porcelain crucible in an electrically heated furnace under ordinary atmospheric conditions at temperature about 1373 K for 2 h to homogenize the melt. The obtained glass samples were quenched into preheated stainless-steel mold preheated at a temperature of about 573 K for 2 h to remove any internal stresses. The samples were then grounded and optically polished to have suitable dimensions (2 cm × 1 cm × 0.15 cm) for the present optical measurements.

X-ray measurements were performed to check the non-crystallinity of the glass samples using a Philips X-ray diffractometer PW/1710 with Ni-filtered, Cu Kα radiation (λ = 1.542 Å) powered at 40 kV and 30 mA. The XRD patterns of the glasses as shown in Fig. 1 did not reveal discrete or any sharp peaks, but the characteristic broad humps of the amorphous materials.

The transmittance (T) and the reflectance (R) optical spectra of the glasses (Fig. 2) were recorded at room temperature in the wavelength range 300–1100 nm using a computerized double beam spectrophotometer, type SHIMADZU UV-2100.

3. Results and discussion

3.1. Determination of optical band gap

The optical absorption coefficient, \( \alpha \), of a material can be evaluated from the optical transmittance, reflectance and the thickness of the sample (d) using the relation:

\[
\alpha = \frac{1}{d} \ln \left( \frac{1-R}{T} \right)
\]  

The absorption coefficient \( \alpha (\nu) \) as a function of photon energy (\( \nu \)) for direct and indirect optical transitions, according to Pankove [17] is given by

\[
\alpha \nu = A_0 \left( \frac{\nu}{E_{opt}} - E_{opt} \right)^p
\]

where \( A_0 \) is an energy-independent constant (band edge steepness parameter in Tauc’s picture [18]). For amorphous materials indirect transitions are valid according to Tauc [18], i.e. power part \( p = 2 \); so, the values of indirect optical band-gap energy (\( E_{opt} \)) can be obtained from Eq. (2) by extrapolating the absorption coefficient to zero absorption in the (\( \alpha \nu \)\(^{1/2} \))– \( \nu \) plot as shown in Fig. 3. The respective values of \( E_{opt} \) are obtained by extrapolating to (\( \alpha \nu \)\(^{1/2} \)) = 0 for the indirect transitions [18,19]. The compositional dependence of \( E_{opt} \) shows a decrease trend as the Bi\(_2\)O\(_3\) and MoO\(_3\) content as shown in Fig. 4. The decreasing values of \( E_{opt} \) can be understood in terms of the structural changes that are taking place in the studied glass system. According to the IR analysis [20], the stoichiometry of the sodium diborate glass, by considering the association of Na\(_2\)O with both MoO\(_3\) and B\(_2\)O\(_3\). Therefore, the BO\(_4\) units will be destroyed and is converted into asymmetric BO\(_3\) units with non-bridging oxygens. Also, the structure of the investigated glasses has distorted [BiO\(_6\)] octahedral units which shift the structural unit [BO\(_4\)] to lower wave numbers, and shifted the band of [BO\(_3\)] unit to higher wave number. This behaviour can be explained as to be due to the formation of new bridging bond of Bi–O–B. This new bond is formed due to the inducement of the electrostatic field of the strongly polarizing Bi\(^{3+}\) ions. The stretching force constant of this bond tends to decrease, since the stretching force constant of Bi–O bonding is lower than that of the B–O bonding. Accordingly, the bond-length of Bi–O
bonding increases, which in turn expand the glass network and replaces B–O linkage by the weaker Bi–O and Mo–O linkages. Thus, the available oxygen environment around the bismuth cations will increase, and this will decrease the values of $E_{opt}^{opt}$.

### 3.2. Determination of the refractive index

According to the theory of reflectivity of light, the refractive index ($n$) as a function of the reflectance ($R$), and the extinction coefficient ($k$) is given by the quadratic equation:

$$R = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2}$$  \hspace{1cm} (3)

The extinction coefficient can be determined from the wavelength ($\lambda$) and the calculated values of $\alpha$ according to the relation:

$$\alpha = \frac{4\pi k}{\lambda}$$  \hspace{1cm} (4)

The refractive index can be well described by a modified Sellmeier dispersion relation (solid lines in Fig. 5):

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} - \frac{D}{\lambda^6} + \frac{E}{\lambda^8}$$  \hspace{1cm} (5)

where $A$, $B$, $C$, $D$ and $E$ are the Sellmeier coefficients are averaged and given in Table 1 for all glasses.

As shown in Eq. (5), the changes in the refractive index are affected by wavelength changes. Fig. 5 shows the plots of the refractive index as a function of the wavelength for the studied glasses. From this figure the refractive decrease with increase the wavelength range of 200–2000 nm. Thus, the compositional dependence of the refractive indices of the studied glasses can be explained as follows. According to the Lorentz–Lorenz equation, the density of the material affects the refractive index in a direct proportion. Also, there are some factors influence on the refractive index such as; the coordination number, $Z$, of the studied glasses can explain its increase as the introducing of the structural units BiO$_6$ and MoO$_6$ as stated previously, on the expense of either BO$_4$ or BO$_3$ will increase the coordination number of the glasses, and creating more NBOs, as noted in IR spectra [20]. This in turn leads to an increase in the average coordination number of the studied glasses, with respect to the base glass sample, which is increasing their index values. Also, the creation of NBOs creates more ionic bonds, which manifest themselves in a larger polarizability over the mostly covalent bonds of bridging oxygen providing a higher index value.

### 3.3. Polarizability and optical basicity of the glasses

The average electronic polarizability of ions and the optical basicity are considered to be from the most important properties of the materials, which is closely related to their applicability in the field of optics and electronics. The optical basicity proposed was used as a measurement of acid–base properties of the oxide glasses, and is expressed in terms of the electron density carried by oxygen. It was found that, optical non-linearity is caused by the electronic polarization of a material upon its exposure to intense light beams, so, the non-linear response of the material is governed by the electronic polarizability. For this purpose, materials with higher optical non-linearity have to be found or designed on the basis of the correlation between the optical non-linearity and with some other easily understandable and accessible electronic properties [21–24].

For isotropic substance such as glasses, the average molar refraction ($R_m$) was given by the Lorentz–Lorenz equation:

$$R_m = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{n^2 - 1}{n^2 + 2} V_m$$  \hspace{1cm} (6)

where the quantity $(n^2 - 1)/(n^2 + 2)$ is called the reflection loss [24,25]. The molar refraction is related to the structure of the glass and it is proportional to the molar electronic polarizability of the material ($\alpha_m$) (in $\times 10^{-24}$ cm$^3$) through the following Clausius–Mosotti relation:

$$\alpha_m = \left( \frac{3}{4\pi N} \right) R_m$$  \hspace{1cm} (7)

where $N$ is Avogadro’s number. For various ternary oxide glasses with the general formula $y_1A_xO_y - y_2B_xO_y - y_3C_xO_y$, where $y’s$ denote the molar fraction of each oxide, the electronic polarizability of oxide ion can be calculated on the basis of refractive indices using the following equation:

$$\alpha_{O^2-}(n) = \frac{[V_m/2.52][n(n^2 - 1)/(n^2 + 2)] - \sum \alpha_{cat}}{N_{O^2-}}$$  \hspace{1cm} (8)

### Table 1

The chemical composition, the refractive index parameters, the molar cation polarizability $\sum \alpha_{cat}$ and the number of oxide ions in the chemical formula ($N_{O^2-}$).

<table>
<thead>
<tr>
<th>Composition (mol%)</th>
<th>Refractive index parameters</th>
<th>$\sum \alpha_{cat}$</th>
<th>$N_{O^2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$</td>
<td>$B$</td>
<td>$C$ ($\times 10^5$)</td>
</tr>
<tr>
<td>0</td>
<td>2.59</td>
<td>2203.46</td>
<td>4.19</td>
</tr>
<tr>
<td>5</td>
<td>2.60</td>
<td>2145.27</td>
<td>4.35</td>
</tr>
<tr>
<td>10</td>
<td>2.99</td>
<td>3627.31</td>
<td>6.72</td>
</tr>
<tr>
<td>15</td>
<td>3.33</td>
<td>4815.91</td>
<td>8.58</td>
</tr>
<tr>
<td>20</td>
<td>3.10</td>
<td>3698.12</td>
<td>7.37</td>
</tr>
<tr>
<td>25</td>
<td>2.48</td>
<td>1232.81</td>
<td>3.96</td>
</tr>
<tr>
<td>30</td>
<td>2.87</td>
<td>2802.81</td>
<td>7.24</td>
</tr>
<tr>
<td>35</td>
<td>3.23</td>
<td>737.87</td>
<td>3.59</td>
</tr>
<tr>
<td>40</td>
<td>3.61</td>
<td>6072.79</td>
<td>12.9</td>
</tr>
</tbody>
</table>
where $\alpha_{\text{O}^2-}$ (n) the electronic polarizability of oxide ion based on refractive indices. $\sum \alpha_{\text{cat}}$ denotes the molar cation polarizability given by $\gamma_1 \rho_{\text{Na}^+} + \gamma_2 \rho_{\text{B}^3+} + \gamma_3 \rho_{\text{C}}$ and $N_{\text{O}^2-}$ denotes the number of oxide ions in the chemical formula given by $\gamma_4 q + \gamma_5 s + \gamma_6 m$. For the studied glasses, the values of both $\sum \alpha_{\text{cat}}$ and $N_{\text{O}^2-}$ were calculated using the values of $\alpha_{\text{Na}^+} = 0.0291 \, \text{Å}^3$ for Na$^+$ ions, of $\alpha_{\text{B}^3+} = 0.002 \, \text{Å}^3$ for B$^3+$ ions and of $\alpha_{\text{Mo}^3+} = 0.169 \, \text{Å}^3$ for Mo$^3+$. The calculated values $\sum \alpha_{\text{cat}}$ and $N_{\text{O}^2-}$ are listed in Table 1. Then the electronic polarizability $\alpha_{\text{O}^2-}$ (n) for different glass compositions easily calculated by using Eq. (8) and figured as a function of wavelength as shown in Fig. 6, this figure shows that the $\alpha_{\text{O}^2-}$ (n) decreases with the increase in the wavelength and increases with the increase in Bi$_2$O$_3$ and MoO$_3$ content. It was reported that Bi$^3+$ cation possesses a very high polarizability, which is due to its large ionic radii and small cation unit field strength. Moreover, Bi$^3+$ ions possess a lone pair in the valence shell. So, the increase in the average polarizability of the studied glasses, on a molar basis, can be attributed to the replacement of a less polarizable boron oxide by a highly polarizable oxides [27,28].

An alternative approach for the calculation of the optical basicity is the determination of the state of polarization of oxide ions in a glass matrix on the basis of refraction data. Duffy [21,22,29] has established the following correlation:

$$A = 1.67 \left(1 - \frac{1}{\alpha_{\text{O}^2-}}\right)$$

The A values were estimated according to Eq. (8). Fig. 7 shows a plot of optical basicity versus the wavelength for different glassy compositions. According to Fig. 7, the values of A decrease with an increase in the wavelength, and increase with an increase in the Bi$_2$O$_3$ and MoO$_3$ content (at any value of the wavelength). Zhao et al. [28] reported that Bi$_2$O$_3$ is a strong acidic oxide with low optical basicity (0.42), while Bi$_2$O$_3$ is an oxide with a significant basicity (1.19). The increased optical basicity of the glasses with large Bi$_2$O$_3$ and MoO$_3$ content indicates that the acidic oxide of Bi$_2$O$_3$ has a significant effect. The low optical basicity means a reduced ability of oxide ions to transfer electrons to the surrounding cations. On the other hand, borate glasses with a large amount of Bi$_2$O$_3$ content possess high optical basicity. High optical basicity means low electron donor ability of the oxide ions.

4. Conclusions

Increasing the Bi$_2$O$_3$ and MoO$_3$ content on the expense of Na$_2$B$_4$O$_7$ in the studied glass system, reveals some remarkable features; as the Bi$_2$O$_3$ and MoO$_3$ content increase, more NBOs were created and the bond-length of the borate structural units increase which in its turn increase the refractive indices, the polarizability, and the optical basicity of the studied glasses. Also, the observed decrease in the optical band gap was related to the weaker bond strength of the Bi–O compared with that of B–O.

Acknowledgements

The authors thank Dr. Shaban I Hussien, Egyptian Atomic Energy Authority for his help in preparing the samples.

References