Spectroscopic studies of xLi$_2$O-(40- x)Bi$_2$O$_3$-20CdO-40B$_2$O$_3$ Glasses

R. Vijaya Kumar, A. Edukondalu, P. Muralimohan, M. Srinivas, K. Siva Kumar

Department of Physics, Osmania University, Hyderabad- 500 007, India.

E-mail: kumar_nizamian@yahoo.co.in

Abstract. Glasses with composition xLi$_2$O-(40- x)Bi$_2$O$_3$-20CdO-40B$_2$O$_3$ where (0 ≤ x ≤ 40) have been prepared using melt quench technique. Optical absorption spectra of the pure glasses revealed that the cutoff wave length decreases and optical band gap ($E_{opt}$) and Urbach energy ($\Delta E$) increases with increase in Li$_2$O content. The $E_{opt}$ values of these glasses are found to be in the range 2.818-3.258 eV where as the values of $\Delta E$ are in the range 0.21-0.33 eV. Raman and infrared spectroscopies have been employed to investigate these glasses in order to obtain information about the competitive role of Bi$_2$O$_3$ and B$_2$O$_3$ in the formation of glass network. IR and Raman spectra show that these glasses are made up of [BO$_3$], [BO$_4$], [BiO$_3$] and [BiO$_6$] units. The formation of Cd in tetrahedral co-ordination was not observed.

1. Introduction
The interest in heavy metal oxide glasses is due to their long infrared cut-off and optical non-linearity [1]. Bismuth based oxide glasses have attracted the attention of scientific community, due to their important applications in the field of glass ceramics, thermal and mechanical sensors etc. a survey of literature shows that there are many reports available on quaternary bismuth borate glasses [2, 3]. The present work is focused on studying the effect of Bi$_2$O$_3$ and Li$_2$O on cadmium borate quaternary glass system. The presence of the two glass formers Bi$_2$O$_3$ and B$_2$O$_3$ increases the interest in present study.

2. Experimental
The optical absorption spectra of the present glass samples (thickness ~1 mm) were recorded at room temperature using a double beam Shimadzu spectrometer (model UV-3100) in the wavelength range 400-800 nm. The uncertainty in the observed wave length is about ±1 nm.

The room temperature Raman measurements were performed in the range 100-2000 cm$^{-1}$ on a micro Raman system from Jobin-Yvon Horiba (LABRAM HR-800) spectrometer. The system is equipped with high stability confocal Microscope for Micro Raman 10×, 50×, 100× objective lens to focus the laser beam. Ar$^+$ laser beam of 488 nm ($E$ = 2.53 eV) was used for excitation. The incident laser power is focused in a dia of ~1–2μm and a notch filter is used to suppress Rayleigh light. In the present system Raman shifts are measured with a precision of ~0.3 cm$^{-1}$ and the spectral resolution is of the order 1 cm$^{-1}$.

Infrared spectra of the powdered glass samples were recorded at room temperature in the range 400–1500 cm$^{-1}$ using a spectrometer (Perkin-Elmer FT-IS, model 1605). These measurements were made on glass powder dispersed in KBr pellets.
3. Results and Discussion

3.1 Optical absorption studies

A distinct cutoff ($\lambda_c$) was observed for each glass sample from optical absorption spectra, $\lambda_c$ decreases with increasing Li$_2$O content. The optical absorption coefficient, $\alpha(\omega)$ of a material can be evaluated from the optical absorption using the relation [4]

$$\alpha(\omega) = \frac{1}{t} \ln \left( \frac{I_o}{I} \right),$$

where ‘t’ is the thickness of each sample and $\ln(I_o/I)$ corresponds to absorbance. The relation between $\alpha(\omega)$ and photon energy of the incident radiation, $h\omega$ is given by the following relation [5]

$$\alpha(\omega) = A_o \left( h\omega - E_{opt} \right)^p / h\omega$$

where $E_{opt}$ is the optical band gap energy in eV, $A_o$ is a constant and $p$ is an index which assumes the values 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for absorption. The values of indirect optical band gap energy $E_{opt}$ can be obtained from expression above by extrapolating absorption coefficient to zero in the $(-\alpha h\omega)^{1/2}$ vs $h\omega$ (Tauc plot) as shown in the figure 1. From table 1, It is observed that the values of $E_{opt}$ increase with Li$_2$O content. This can be understood in the terms of structural changes that are taking place with the introduction of Li$_2$O into the glass.

![Figure 1. Tauc plots of present glasses.](image1)

![Figure 2. Urbach plots of present glasses.](image2)

The relation between $\alpha(\omega)$ and Urbach energy ($\Delta E$) is given by the well known Urbach law given by the relation

$$\alpha(\omega) = \text{const.} \exp(h\omega - \Delta E),$$

$\Delta E$ is usually interpreted as the width of the tail of the localized stare in the band gap. The above equation can be rewritten as

$$\ln \alpha(\omega) = \frac{h\omega}{\Delta E} - \text{const.}$$

Urbach plots are the plots where the natural logarithm of absorption coefficients, $\ln \alpha$, is plotted against photon energy, $h\omega$. Urbach plot for a typical glass sample is shown in the figure 2. The values of Urbach energy ($\Delta E$) were calculated by determining slopes of the linear regions of the curves and taking their reciprocals. The probable error in ($\Delta E$) is found to be $\pm 0.001$ eV. It is found that Urbach energy decreases with increase in the Li$_2$O content in the present glass system shown in table 1.

| Li$_2$O mol% | $\lambda_c$ (nm) | $E_{opt}$ (eV) | $\Delta E$ (eV) |
|--------------|-----------------|---------------|----------------|
| $x=0$        | 381             | 2.818         | 0.21           |
| $x=10$       | 375             | 2.901         | 0.23           |
| $x=20$       | 370             | 2.999         | 0.28           |
| $x=30$       | 354             | 3.104         | 0.30           |
| $x=40$       | 295             | 3.258         | 0.33           |

Table 1: $\lambda_c$, $E_{opt}$, $\Delta E$ values of -(40- $x$)Bi$_2$O$_3$-20CdO-40B$_2$O$_3$ where (0 $\leq$ $x$ $\leq$ 40) glasses.
3.2 Raman and IR studies

Figure 3 shows the Raman spectra of $x\text{Li}_2\text{O}-(40-x)\text{Bi}_2\text{O}_3-20\text{CdO}-40\text{B}_2\text{O}_3$, $0 \leq x \leq 40$ glasses. In the present glasses the band was observed in the range 140-145 cm$^{-1}$ and its intensity decreases with increasing Li$_2$O content. Therefore we assume that Bi$^{3+}$ cations are incorporated in [BiO$_3$] and [BiO$_6$] groups. This is confirmed by the presence of bands in the present IR spectra (figure 4) around 498 cm$^{-1}$ can be assigned to stretching vibrations of Bi-O bonds in strongly distorted vibrations BiO$_6$ units [3, 6]. In the present study this band shifts from 498 cm$^{-1}$ to higher wavenumbers with increasing Li$_2$O content, which is due to the change of local symmetry in [BiO$_n$] polyhedra. Similar observations were found in Bi$_2$O$_3$-B$_2$O$_3$-ZnO-Li$_2$O, Bi$_2$O$_3$-B$_2$O$_3$-Li$_2$O [1, 7] glasses and the band 878 cm$^{-1}$ is assigned to symmetric stretching vibrations of Bi-O bonds in BiO$_3$ units, and stretching vibrations of B-O bonds in BO$_4$ units from diborate groups. The broad absorption band around 995 cm$^{-1}$ in the present IR spectra assigned to stretching vibrations of B-Ø bonds in BO$_4$ units from tri-, tetra- and pentaborate groups [8, 9]. The broad but strong band occurring in the present Raman spectra around 338 cm$^{-1}$ can be attributed to the Bi-O bonds strongly distorted in BiO$_6$ units and the band around 416 cm$^{-1}$ is assigned to the Bi-O-Bi bending vibrations in BiO$_6$ units, while the shoulder at 566 cm$^{-1}$ can be attributed to Bi-O stretching vibrations of [BiO$_6$] units [1, 7, 8]. In Raman spectra at Li$_2$O ≥ 20 glasses, new bands arises around 508 cm$^{-1}$, may be attributed to the Bi-O vibrations in BiO$_6$ and the band around 725 cm$^{-1}$ is attributed to the vibrations of chain type metabolate groups [8].

In Raman spectra the strong band observed around 929 cm$^{-1}$ can be assigned to vibrations of orthoborate groups [1, 10]. It is observed that the intensity of this band remains constant this is because the B$_2$O$_3$ content remains constant in the glass system. Assignment has been suggested for 1274 cm$^{-1}$ band in the Raman spectra of pyroborate groups, involving primarily the stretching of the terminal B-O' bonds [11, 12]. This is confirmed from the fact that in the present glasses, the band observed at 700-712 cm$^{-1}$ in infrared spectra is assigned to B-O-B bending vibrations in [BO$_3$] triangles while the strong bands in the range 1195 cm$^{-1}$ is assigned for stretching vibrations of B-O bonds in BO$_3$ units from meta and ortho-borate groups [8] and 1365 cm$^{-1}$ arises from B-O' bonds stretching in BO$_3$ units from varied types of borate groups respectively [9, 13, 14].

As the expense of the Bi$_2$O$_3$ content i.e at high Li$_2$O composition of glass 40Li$_2$O-20CdO-40B$_2$O$_3$ in IR spectra the band around 508 cm$^{-1}$ can be assigned to O-B-O bond bending vibrations of various borate segments the next one centered at 712 cm$^{-1}$ is assigned to the O$_2$B-O-BO$_3$ bands in bending vibrations [15] and the band 890 cm$^{-1}$ which is a characteristic for stretching vibrations of B-O bonds in BO$_4$ tetrahedra from diborate groups [16, 17] and a band centered at 1025 cm$^{-1}$ assigned to B-O bonds stretching vibrations in BO$_4$ tetrahedral (O: oxygen atom bridging two boron atoms) from tri-, tetra- and penta- borate groups [16, 17]. The bands around 1215 cm$^{-1}$ is due to the stretching vibrations of B-O' bonds in BO$_3$ units from meta and ortho borate groups and 1397 cm$^{-1}$ assigned to asymmetric stretching mode of borate triangles with (BO$_3$, BO$_2$O) and stretching vibrations of the
borate triangles with non-bridging oxygen (NBO) in various borate groups [13, 16]. In Raman spectra the bands at 333 cm$^{-1}$, 419 cm$^{-1}$ and 507 cm$^{-1}$ are assigned to tetrahedral borate groups mainly pentaborate and tri borate groups [17]. The band situated at 764 cm$^{-1}$ has been attributed to the symmetrical breathing vibrations of six-member borate rings with one or two BO$_4$ tetrahedra [13]. The band at 950 cm$^{-1}$ is assigned to vibrations of diborate groups and 1150 cm$^{-1}$ is assigned to vibrations of pyro-borate groups [16] and the band 1304 cm$^{-1}$ is assigned to B-O$^-$ vibrations from various borate groups the presence in our Raman spectra of the band at 1443 cm$^{-1}$ assigned to vibrations of the chain type metaborate units [18].

In all glass samples except in 40B$_2$O$_3$-20CdO-40Bi$_2$O$_3$ glass sample the weak bands at 438 m$^{-1}$ and 463 cm$^{-1}$ in IR spectra were attributed to the Li-O-Li and Li-O-Bi/B bonds [7]. In the present glass system the band at 806 cm$^{-1}$ indicates the absence of boroxal ring formation and the band at 840 cm$^{-1}$ is not observed in which suggest that the formation of tetrahedral co-ordination of Cd (CdO$_4$) is absent [2, 19]. The low frequency band around 452 cm$^{-1}$ (weakly observed) in the IR spectra and Raman peak at 266 cm$^{-1}$ observed in all glass samples may be attributed to the Cd-O vibrational modes of metal cation Cd$^{2+}$ [19].

4. Conclusions

In the present glass samples it is observed that cutoff wave length($\lambda_c$) decreases with increasing Li$_2$O and The values of $E_{opt}$ and $\Delta$E depends on Li$_2$O concentration and increases with Li$_2$O content. The present glasses are made up of [BiO$_3$], [BiO$_6$][BO$_3$] and [BO$_4$] units. In the present glass system there is no formation of tetrahedral co-ordination CdO$_4$ units and CdO acts as network modifier in present glasses.

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