International Journal of Engineering Research-Online
A Peer Reviewed International Journal
Articles available online http://www.ijoer.in

Vol.3., S3, 2015

NCERFM-2015

ISSN: 2321-7758

OPTICAL AND IR STUDIES OF BINARY BISMUTH BORATE GLASSES

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ABSTRACT

Six compositions of binary bismuth borate glasses xBi_2O_3-(100-x) B_2O_3 (x in mol %, ranging from 25 to 50 in steps of5) were prepared using melt quenching method. Optical absorption and infrared (IR) studies were carried out for these samples. Optical band gap (E_{opt}) values are found to decrease with increase in the concentration of Bi_2O_3, indicating the loosening of glass network. The optical band gap values calculated from absorption spectrum fitting (ASF) method are in agreement with the values calculated from Tauc's plots. The parameters such as refractive index (n), molar refraction (R_m), molar electronic polarizability (α_m), metallization parameter (M) of these glasses were evaluated. IR studies revealed the presence of [BiO_6], BO_3 trigonal and BO_4 tetrahedral structural units in these glasses. The IR spectral analysis of the present glass system shows that Bi^{3+} cations are incorporated in the glass network as [BiO_3] pyramidal and [BiO_6] octahedral units. IR spectra show that the number of non-bridging oxygens (NBOs) increases with the increase in Bi_2O_3 content.

Keywords: optical absorption, glass network, infrared, optical band gap, refractive index and molar refraction

1. INTRODUCTION

Bismuth oxide glasses have many applications including as γ-ray absorbers, in scintillation detectors for high energy physics. The large polarizability and small field strength of Bi^{3+} in oxide glasses makes them suitable for optical devices such as optical isolators, optical switches, optical kerr shutter, high refractive index materials, etc. [1].Borate rich glasses containing heavy metal oxides such as Bi_2O_3 have wide applications as laser hosts, lamp phosphors and other photonic devices [2].

According to Narayana Reddy and Sreekanth Chakradhar [3], in borate glasses, the structure of pure vitreous B_2O_3 consists of a random network of boroxyl rings and BO_3 triangles connected by B-O-B linkage. The addition of heavy metal oxide like Bi_2O_3 loosens the network and transforms the structure into BO_4 tetrahedral units.

The present glass system is prepared using melt quenching technique. The physical and some of the optical parameters of the present glass system were evaluated earlier by the same authors and presented in the earlier publication [4]. The objective of the present work is to calculate the optical band gap using ASF method and also the structural changes in the glass network by infrared analysis. The optical parameters such as refractive index (n), molar refraction (R_m), molar electronic polarizability (α_m), metallization parameter (M) of these glasses were evaluated. The effect of Bi_2O_3 on these optical parameters and structural changes with the composition of Bi_2O_3 has been studied.

2. Experimental

The glasses were prepared by conventional melt quenching technique and melted in the range 850-865 ^oC [5]. The obtained glasses were transparent. These glass samples were annealed for about 15 hrs at 200^oC to remove thermal strains. The glasses xBi_2O_3-(100-x) B_2O_3 are labeled as BB1, BB2, BB3, BB4, BB5 and BB6 for x= 25, 30, 35, 40, 45 and 50 mol% of Bi_2O_3 respectively.

Fig.1 shows the X-ray diffraction (XRD) spectra of typical BB2 glass sample. Similar XRD pattern was observed for other glass samples. The absence of Bragg's peaks in XRD patterns confirms the amorphous nature of the glasses. The optical absorption spectra were recorded at room temperature using a double beam shimadzu spectrometer (model UV-3101 PC) in the wavelength range 300 to 450 nm with the sample thichness around 0.8 µm. The Infrared spectra of the powdered glass samples were recorded at room temperature in the

range 400– 2000 cm^{-1} using a spectrometer (Perkin- Elmer FT-IS, model 1605). These measurements were made on glass powder dispersed in KBr pellets.

Table 1. Optical parameters of the glass system xBi_2O_3-(100-x) B_2O_3

Parameter (± error limits)	x=25 BB1	x=30 BB2	x=35 BB3	x=40 BB4	x=45 BB5	x=50 BB6
Optical band gap, E_{opt} (eV) (± 0.005)	3.338	3.306	3.173	3.14	3.048	3.025
Optical band gap, E_{opt}^{asf} (eV) (±0.005)	3.199	3.161	3.099	3.037	2.889	2.864
Refractive index, n (±0.002)	2.311	2.319	2.352	2.360	2.384	2.390
Avg. molar refraction, R_m cm^3/mol (±0.001)	21.216	22.348	22.997	23.788	25.921	26.680
Molar polarizability, α_m x 10^{-24} cm^3 (±0.001)	8.415	8.864	9.121	9.435	10.281	10.582
Metallization parameter, M	0.408	0.406	0.398	0.396	0.390	0.389

Table 2. Band positions and corresponding assignments of IR spectra of all glass compositions.

Bands and Shoulders	Assignment
~ 450 cm^{-1}(w) and ~ 465-530 cm^{-1} (w)	Bi-O vibrations
~ 665-705 cm^{-1}(s)	The bending vibration of B-O-B linkages of BO_3 units
Shoulder at 840 cm^{-1}	Symmetrical stretching vibration of the Bi-O bonds in the $[BiO_3]$ groups
~ 990-933 cm^{-1}(s)	Presence of diborate units of BO_4 groups
Shoulder at 1340 cm^{-1}	B-O-B stretching vibrations of $(BO_3)^{3-}$ units
~1455 and 1540 cm^{-1}(s)	Asymmetric stretching of B-O bond of the BO_3 units
~ 1650-1684 cm^{-1}(w)	Bending vibration of OH groups

3. Results and discussion

3.1 Optical absorption

The optical absorption spectra of a typical glass sample BB2 is shown in Fig.2. The cutoff-wavelength (λ_{cutoff}), optical band gap (E_{opt}) and Urbach energy (ΔE) values of the present glass samples are evaluated and presented in an earlier publication [4] from this laboratory.

E_{opt} values were evaluated from the Tauc's plots as shown in Fig.3. Tauc's plots are the plots of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ where $\hbar\omega$ is the photon energy of the incident radiation and α is the absorption coefficient. In this method of evaluation for the absorption coefficient the thickness of the sample is required [5]. E_{opt} values can also be measured even if the thickness of the sample is not known by an alternate method called absorption spectrum fitting (ASF) method proposed by Escobar-Alarcon et al.[6] and Dariush Souri and Shomalian [7]. The values of E_{opt} using ASF method, (E_{opt}^{asf}) can be determined by extrapolating the linear regions of the curve $(a/\lambda)^{1/2}$ versus $(1/\lambda)$ at $(a/\lambda)^{1/2}$ =0 where a is the absorbance and λ is the wavelength. E_{opt}^{asf} in eV can be obtained from the parameter λ_g using the expression

$$E_{opt}^{asf} = \frac{1239.83}{\lambda_g} \quad \text{..... (1)}$$

where λ_g is the wavelength corresponding to the optical band gap. These values are presented in Table 1. The variation of $(a/\lambda)^{1/2}$ versus $(1/\lambda)$ for the sample BB2 is shown in Fig. 4.

It is clear from Table 1 that the values of E_{opt} obtained from Tauc's plots matches well with the E_{opt}^{asf} values calculated from ASF method. The optical band gap values are found to decrease with increase in the concentration of Bi_2O_3, which indicates that the glass network becomes less tightly packed and hence degree of disorder increases.

3.2 Refractive index

The refractive index (n) is determined from the E_{opt} values using the relation proposed by Dimitrov and Sakka [8]

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_{opt}}{20}} \qquad \text{..... (2)}$$

The refractive index values calculated using equation (2) are presented in Table 1. Refractive index values increases with the increase in the content of Bi_2O_3.The variation in n values is small indicating no significant changes in the glass network. The increment in refractive index is assigned to increase in density.

3.3 Molar polarizability

The average molar refraction, R_m is given by the Lorentz-Lorentz equation[9]

$$R_m = \left[\frac{n^2-1}{n^2+2}\right] V_m \qquad \text{..... (3)}$$

where the $[(n^2-1)/(n^2+2)]$ is called the reflection loss and V_m is the molar volume. According to the Clausis-Mosotti relation molar polarizability of the materials ($\alpha_m \times 10^{-24}$ cm^3) is given by the relation

$$\alpha_m = \left[\frac{3}{4\pi N}\right] R_m \qquad \text{.....(4)}$$

where N is the Avogadro's number. The values of molar refraction and molar polarizability are presented in Table1. The increase in molar refraction and refractive index with increase in content of Bi_2O_3 leads to the increase in molar polarizability. It is clear that the refractive index of the present glasses not only depends on the density values but also on the polarizability values of the glasses. So the incresase of Bi_2O_3, being heavy metal oxide, content in the glasses is the cause for the increase of molar polarizability.

3.4 Metallization parameter

A condition for predicting metallic or insulating behavior in the condensed state matter is metallization criterion [10]. The metallization parameter, M is given by

$$M = 1 - (R_m/V_m) \qquad \text{..... (5)}$$

If M>1, then the materials show metallic nature and if M<1 they exhibit insulating behavior. The values of M of the present glasses are given in Table 1 and are found to be less than one for all the glass compositions. This shows that the present glasses are poor electronic conductors.

3.5 IR spectra

Infrared spectra of all the glass samples are shown in Fig.5. The IR spectra show seven peaks containing weak (w), medium (m) and strong (s) bands. Usually the borate glass has three vibrational bands at 1200-1600, 800-1200 and at ~ 700 cm^{-1}. Glasses containing Bi_2O_3 have four fundamental vibrations at ~ 830, ~ 620, ~ 450 and 350 cm^{-1} [5].

The bands and shoulders observed in the IR spectra of the glass samples are assigned to their respective vibrations and are given in Table 2. The weak band observed at ~ 1650- 1684 cm^{-1}indicates the presence of crystal water with H-O-H bending mode of vibration. The weak band around 1455 cm^{-1} and absorption peak at 1540 cm^{-1} is due to B-O asymmetric stretching vibrations of $(BO_3)^{3-}$ units [5]. The shoulder around 1340 cm^{-1} is due to the B-O-B stretching vibrations of BO_3 units in orthoborate and pyroborate groups [11]. The broad and strong band at 990-933 cm^{-1} indicates the presence of diborate units of BO_4 groups and formation of non-bridging oxygens (NBOs) [12]. The shoulder around 840 cm^{-1} is attributed to the symmetrical stretching vibration of Bi-O bonds in the $[BiO_3]$ groups. The strong absorption band in the range 665-705 cm^{-1} is due to the bending of B-O-B linkages of BO_3 units in the borate network [5]. The weak bands in the range 465-530 cm^{-1} and around 450 cm^{-1} are attributed to the doubly degenerate bending vibrations of $[BiO_3]$ pyramidal units and $[BiO_6]$ polyhedral units respectively [13,14].

The shoulder around 840 cm^{-1} and the band 933-990 cm^{-1} became more predominant with the increase of Bi_2O_3 content. As the content of Bi_2O_3 increased the disorder in the glass matrix increased and this may be due to the formation of NBOs. The increase in Bi_2O_3 content in the present glass system transforms the structure into a bismuthate one consisting of $[BiO_6]$ and $[BiO_3]$ groups. Borate glasses consist of random

network of planar BO_3 triangular units along with boroxol rings [15]. But in the present glass system there is no peak observed at 806 cm^{-1} which is the characteristic frequency of boroxol ring. Hence from the IR spectra it is evident that the present glasses consists of $[BiO_6]$ and $[BiO_3]$ groups and randomly connected trigonal BO_3 and tetrahedral BO_4 structural units with the absence of boroxol rings.

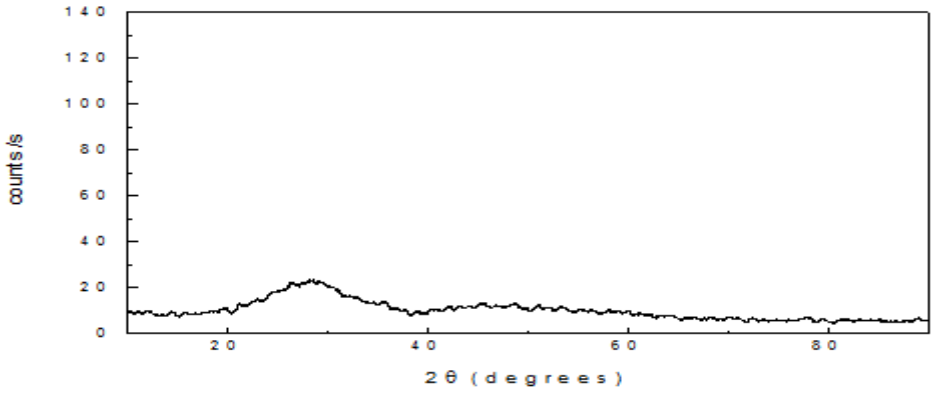

Fig.1. XRD spectra of BB2 glass sample

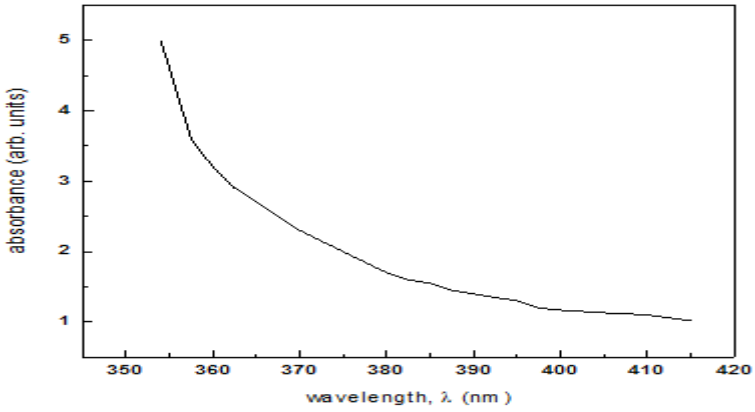

Fig.2. Optical absorption spectrum of BB2 glass sample

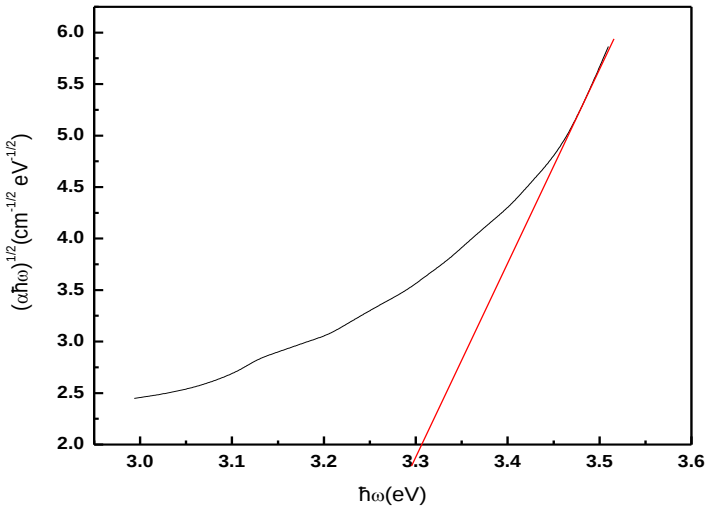

Fig. 3. $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy, $\hbar\omega$ for BB2 glass sample

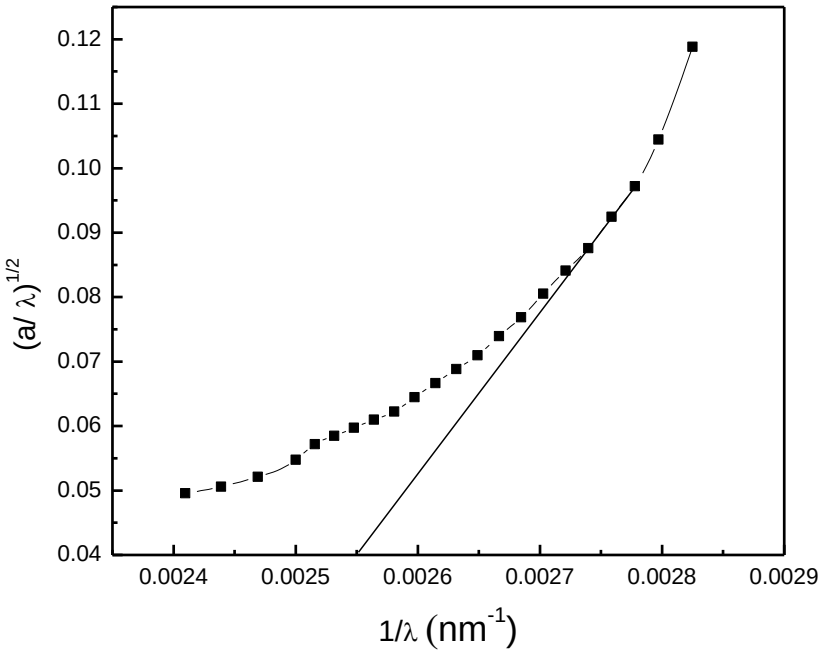

Fig.4 (a/λ)1/2 verses (1/λ) (ASF) of BB2 glass sample

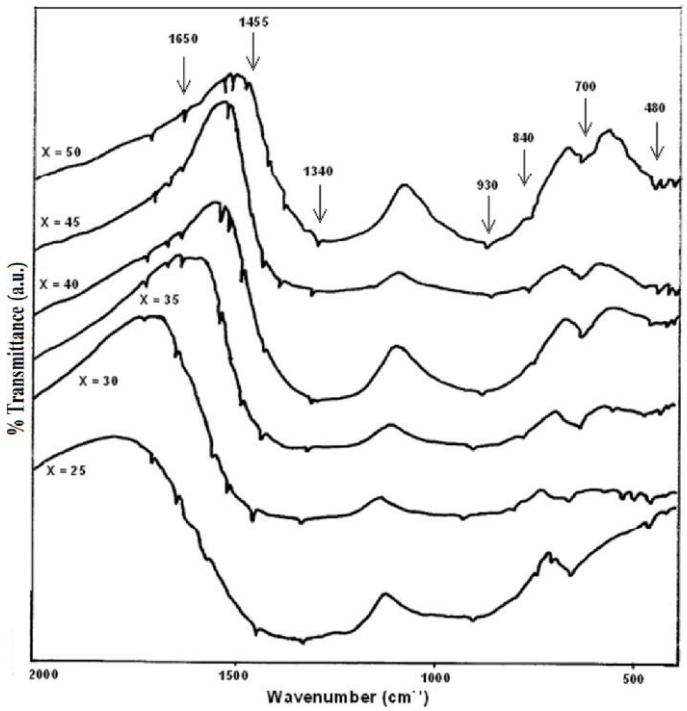

Fig.5. Infrared spectra of xBi_2O_3-(100-x) B_2O_3
(x in mol %, ranging from 25 to 50 in steps of 5) glasses

Conclusions

The decrease in the values E_{opt} indicates that the glass network becomes less tightly packed and degree of disorder increases with increase of concentration of Bi_2O_3. This fact has been supported by IR studies in which the number of non-bridging oxygens (NBOs) increases with increase in the content of Bi_2O_3. The optical band gap values calculated from ASF method are in agreement with the values calculated from Tauc's plots. The infrared spectral analysis of the present glass system shows that Bi^{3+} cations are incorporated in the

glass network as [BiO_3] pyramidal and [BiO_6] octahedral units.

Acknowledgements:

The authors (D.Saritha and G.Bhikshamaiah) wishes to thank Head, Department of physics, Osmania University for providing experimental facilities.

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