

# Effect of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> on the Spectroscopic and Thermal Properties of Bismuth Borate Glasses

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**ABSTRACT**— Glass samples from three  $x \text{ Bi}_2\text{O}_3$ -  $y \text{ SiO}_2$  -  $(100-x-y) \text{ B}_2\text{O}_3$ , (Where  $x = 50$  and  $y = 5, 10, 20$ ) and  $x \text{ Bi}_2\text{O}_3$ - $y \text{ SiO}_2$ - $z \text{ Al}_2\text{O}_3$ -  $(100-x-y-z) \text{ B}_2\text{O}_3$  (Where  $x=50$ ,  $y= 0,5$  and  $30$ ,  $z=2,4,6,8$ ) were prepared by melt quenching technique.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  substituted bismuth borate ( $\text{Bi}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{B}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ ) glasses were prepared with varying concentrations of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , the characterization of these glasses was carried out using density measurements. The absorption edge, Urbach energy and transition temperature has been calculated from the optical and thermal analysis respectively. The structural analysis reveals that the glass has BO<sub>4</sub>, BO<sub>3</sub> units as the local structure. The molar volume of glasses has also been calculated from density measurements following Archimedes method, which clearly shows decrease in molar volume of bismuthborosilicate and increase in borosilicate glasses. DSC and density measurements supports the conclusions drawn from these studies.

**Keywords**— Glass formation, Glass transition, Glasses, Optical properties, DSC measurements

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## 1. INTRODUCTION

On borate glasses lot of work has been going on during last decades, especially concerning on optimization of glass preparation, investigation of properties and efforts to acquire information about the structure of glasses [1, 2]. Heavy metal oxide glasses have attracted interest because of their optical properties such as refractive indices, large third order nonlinear response in second harmonic generation and infrared transmittance [3-8]. Combining bismuth oxide with boric oxide, allows to tune the optical properties in a wide range depending on the composition. Boric acid  $\text{B}_2\text{O}_3$ , acts as one of the most important glass formers and flux materials. Melts with composition rich in  $\text{B}_2\text{O}_3$  exhibit high viscosity and tend to the formation of glasses [9-10]. The structure of vitreous  $\text{B}_2\text{O}_3$  is modeled in two different ways. In the first model  $\text{B}_2\text{O}_3$  glass is considered as a continuous random network of three coordinate borons and addition of alkali or alkaline earth oxide results in the formation of four coordinate borons with the modifier ions filling the interstices. In the second model vitreous  $\text{B}_2\text{O}_3$  consisted entirely of boroxyl rings and addition of modifier oxide results in the formation of superstructural units like pentaborate, triborate and diborate groups [11-12]. Adding  $\text{Al}_2\text{O}_3$  to the borate glasses produces interesting structural effects and also effects chemical durability. In the present work, glasses of the system  $\text{Bi}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{B}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  has been prepared and the effects of substitution of  $\text{B}_2\text{O}_3$  by  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  on various properties, including density have been investigated.

## 2. EXPERIMENTAL TECHNIQUES

Glass samples from the three series  $x \text{ Bi}_2\text{O}_3$ -  $y \text{ SiO}_2$  -  $(100-x-y) \text{ B}_2\text{O}_3$ , (Where  $x = 50$  and  $y = 5, 10, 20$ ) and  $x \text{ Bi}_2\text{O}_3$ - $y \text{ SiO}_2$ - $z \text{ Al}_2\text{O}_3$ -  $(100-x-y-z) \text{ B}_2\text{O}_3$  (Where  $x=50$ ,  $y= 0,5$  and  $30$ ,  $z=2,4,6,8$ ) were prepared by melt quenching technique. The starting materials were  $\text{H}_3\text{BO}_3$  (Merck, 99.99 %),  $\text{SiO}_2$  (CDH, India, 99.5%),  $\text{Bi}_2\text{O}_3$  (Sigma Aldrich 99.99%) and  $\text{Al}_2\text{O}_3$  (CDH, India, 99.5%). Appropriate amounts of these starting materials were weighed and thoroughly mixed and ground in an agate mortar–pestle for about an hour. The batch mixture was then transferred to a platinum crucible sintered in an electric furnace at 450 °C temperature for 24 hours, and the furnace temperature was then slowly raised to 950 °C. The melt was heat-treated at 950 °C for about 30 minutes before quenching it on a heavy brass block. The disk shaped glass samples obtained was then quickly transferred to another furnace previously kept at 350 °C. It was annealed in this furnace for 30 mins to reduce thermal stresses generated inside glass by its rapid quenching. All glass samples were disk shaped. The opposite faces of the samples were ground and polished with different grades of emery powder for UV-visible spectroscopy measurements.

The density of all 11 samples were measured by Archimedes principle with an accuracy and precision of  $\pm 0.006 \text{ g cm}^{-3}$ . Density values were used to calculate glass molar volume,  $V_m = M/d$  where, d is the density and M is its molecular weight Excess volume ( $V_x$ ) is also calculated from the crystal volume ( $V_0$ ) and molar volume i.e.  $V_x = V_m - V_0$ .

UV-Visible absorption spectra were recorded on all polished disk shaped glass samples in the wavelength range of 200 to 800 nm on a Shimadzu Double Beam Spectrophotometer (Model 1601). The absorption coefficient,  $\alpha(\lambda)$ , was determined from the relation:

$$\alpha(\lambda) = \ln(100/T)/t$$

Where t is the sample thickness (cm), T the transmittance (%) and  $\ln(100/T)$  corresponds

to absorbance. Fig 1 and 2 shows the Urbach plots for the samples of the glass series given in table 1. In these graphs, we have plotted  $\ln(\alpha)$  against photon energy, the linear region of which directly gives the value of absorption edge and the reciprocal of the slope of the linear regions is Urbach Energy.

**Table 1:** Composition, Density, Molar Volume, Excess Volume, Absorption Edge, and Urbach Energy

Sample No.	Composition (Mol %)				Density (gm/cm <sup>3</sup> )	Molar Vol $V_m$	Crystal Volume $V_0$	Excess Vol $V_x$	Absorption Edge $E_0$ (eV)	Urbach Energy $\Delta E$ (eV)
	Bi <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>						
740	50	45	5	-	6.985	38.26	44.73	6.47	1.96	0.54
744	50	40	10	-	7.118	37.48	44.17	6.69	2.03	0.42
748	50	30	20	-	7.162	37.12	43.04	5.92	2.21	0.46
1063	50	48	-	2	7.002	38.33	45.04	6.71	2.55	0.22
1065	50	46	-	4	6.960	38.66	44.78	6.12	2.42	0.24
1067	50	44	-	6	6.961	38.74	44.54	5.80	2.49	0.23
1069	50	42	-	8	6.894	39.21	44.28	5.07	2.45	0.26
1071	50	43	5	2	6.965	38.47	44.48	6.01	2.39	0.31
1073	50	41	5	4	6.993	38.41	44.23	5.82	2.01	0.52
1075	50	39	5	6	6.882	39.12	43.97	4.85	2.15	0.43
1077	50	37	5	8	6.872	39.27	43.72	4.45	2.27	0.38

DSC measurements were carried out on all glasses on a Perkin Elmer DSC-7 system in the temperature range of 200-730 °C with a heating rate of 10<sup>0</sup>C/min. DSC studies were performed on powdered glass samples in Platinum pans. We use sample amounts of 20-50 mg for recording the spectra. Table 2 gives the detail of glass transition (inflection point), crystallization (peak point) and melting temperatures of all the glass samples.

**Table 2.** Values of  $T_g$ ,  $T_c$ ,  $T_m$ ,  $K_{gl}$  and  $T_{rg}$  calculated from DSC thermograms taken at 10<sup>0</sup>C/min heating rate

Sample No.	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$T_c - T_g$ (°C)	$T_m - T_c$ (°C)	$T_c - T_g / T_m - T_c$ (°C)	$T_g / T_m$ (°C)
740	403	484	637	81	153	0.53	0.63
744	397	477	630	80	153	0.52	0.62
748	396	500	634	104	134	0.78	0.62
1063	397	479	627	82	148	0.55	0.63
1065	397	489	579	92	90	1.02	0.68
1067	391	479	579	88	100	0.88	0.67
1069	390	475	585	85	110	0.77	0.67
1071	404	509	529	105	20	5.25	0.76
1073	400	525	625	125	100	1.25	0.64
1075	395	456	621	61	165	0.37	0.64
1077	397	447	583	50	136	0.37	0.68

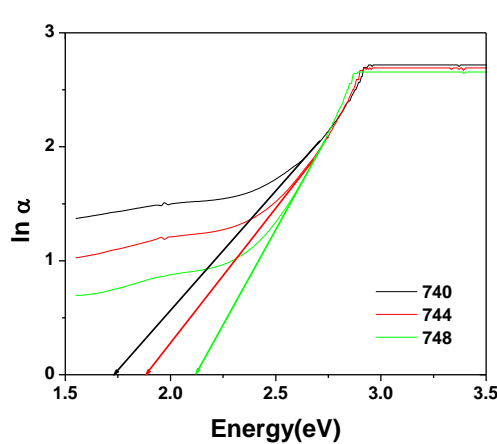
### 3. RESULTS AND DISCUSSIONS

The densities of all the glasses are tabulated in Table 1. From the results it can be seen that the values of the density increases with the addition of SiO<sub>2</sub> in borosilicate and decreases with the addition of Al<sub>2</sub>O<sub>3</sub>. The addition of SiO<sub>2</sub> will modify the glass structure by creating a non-bridging oxygen (NBOs) in the network. The NBOs created were believed to alter the glass structure in a way that the packing of the molecules becomes denser as more network modifier ions attempt to occupy the interstices within the network [13].

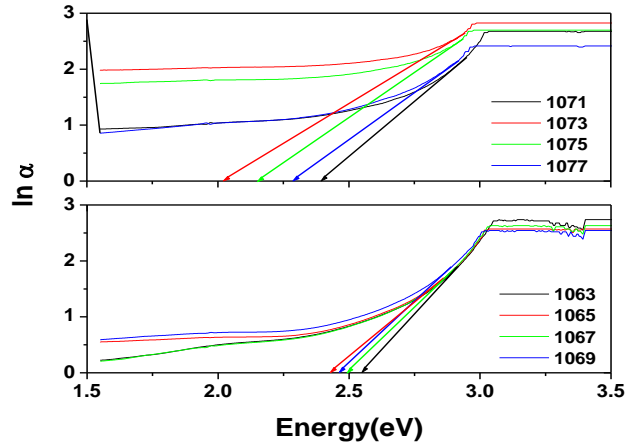
The optical absorption spectra of the glass samples were measured in the wavelength region 200-800 nm and Urbach plots are shown in figs. 1 and 2. The absorption coefficient  $\alpha(\nu)$  in amorphous materials in the optical region near the absorption edge at a particular temperature, obeys an empirical relation known as Urbach's rule given by

$$\alpha(\nu) = \alpha_0 \exp(h\nu / \Delta E_0)$$

where  $h\nu$  is the photon energy,  $\alpha_0$  is constant and  $\Delta E_0$  an energy which is interpreted as the width of the localized state in the normally forbidden band gap and which is also known as Urbach energy [14].



**Fig 1.** Urbach plot for bismuth borosilicate glasses



**Fig 2.** Urbach plot for bismuth borosilicate and aluminosilicate glasses

It is seen that the glass samples show strong absorption in UV region. The tail of the band is trailing into the visible region. Optical absorption in solids occurs by a mechanism that involves the coupling of the electric field of the incident radiation to the dipole moment in the material and the consequent transfer of energy [15].

According to the Stevels, the absorption edge in oxide glasses corresponds to the transition of an electron belonging to an oxygen ion to an excited state. The more weakly these electrons are bound, the more easily absorption occurs [16]. The energy gap increases with the increase in concentration of  $\text{SiO}_2$  in borosilicate but decreases with the increase in the concentration of  $\text{Al}_2\text{O}_3$  in boroaluminate and in boroaluminosilicate glasses. Arbuzov, Stevels and Mcswain et. Al suggested that in oxide glasses the shift of energy gap to lower energy could be related to the formation of non-bridging oxygen [14,17,18]. Duffy explained the ultraviolet transparency of oxide glasses in terms of electronegativity of the constituent oxygen atoms. In glasses, negative charges on the negative have larger magnitude than that on the bridging oxygen's. Increasing the ionicity of oxygen ions by converting them from bridging to non-bridging oxygen (NBO) ions, raises the top of the valence band resulting in the reduction of band gap energy ( $E_g$ ). Hence, ultraviolet absorption occurs at lower photon energies, as the oxygen atom becomes NBO [19].

The observed variations in the optical energy gap with the increase in  $\text{SiO}_2$  in the present study can be explained by considering the changes in the glass structure because of expansion of the glass network.

The optical energy gap shifted toward longer wavelength as more  $\text{Al}_2\text{O}_3$  was substituted for  $\text{B}_2\text{O}_3$  in boroalumino and boroaluminosilicate glasses, the network becomes systematically weakens and a more open network with NBO's was formed. NBO's in the glass network shifted the fundamental absorption edge towards longer wavelength side.

The Urbach rule for absorption coefficient is an attempt to explain the observed exponential tail in terms of internal electric fields generated within the exponential broadening of the energy states. Dexter and Redfield have qualitatively shown that such a tailing off of states could modify the direct band transition and cause an exponential energy dependence on the intrinsic edge [20,21]. The average value of the band tailing energy  $\Delta E_0$  (table1) 0.47eV for borosilicate, 0.23eV boroaluminate and 0.41eV for boroaluminosilicate glass samples in the present study.

The ease in glass formation is determined by calculating the reduced glass transition temperature  $\text{Trg} = \text{Tg}/\text{Tm}$  [28]. The value obtained obey the two-thirds rule which states

$$\text{Tg}/\text{Tm} = 2/3$$

$\text{Tg}/\text{Tm}$  holds good for these composition.

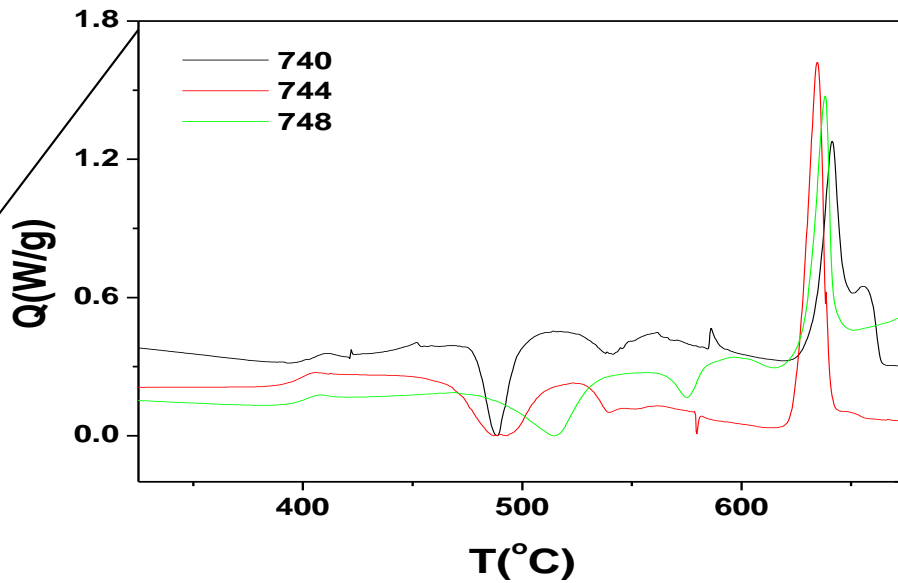


Fig 5. DSC plot for Bismuth borosilicate glasses

The difference between  $T_c$  and  $T_g$ , which is an indication of thermal stability of glasses against crystallization increases with increase in  $SiO_2$  content in bismuth borosilicate glasses. The glass forming parameter is calculated using Hruby's parameter [29]

$$K_{gl} = (T_c - T_g) / (T_m - T_c)$$

Fig 5, 6 and 7 show the DSC traces for bismuth borosilicate, bismuth boroaluminosilicate and boroaluminosilicate glasses during the first heating cycle. We can in boroaluminosilicate glasses, the glass forming ability increases at 4 mol% of  $Al_2O_3$  and above 4 mol% it decreases, similar effects are observed in bismuth boroaluminosilicate glasses.

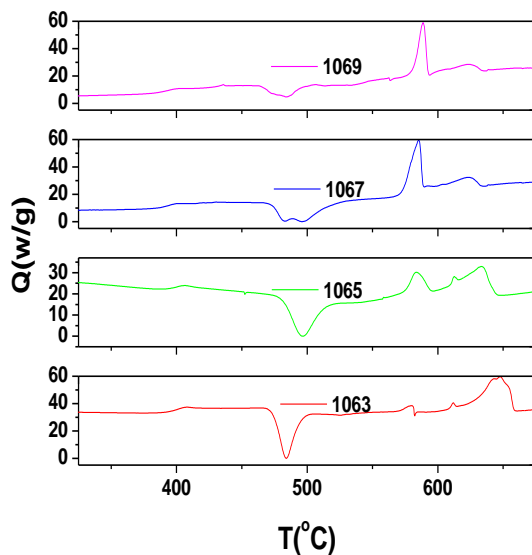


Fig6: DSC plots for bismuth boroaluminosilicate glasses

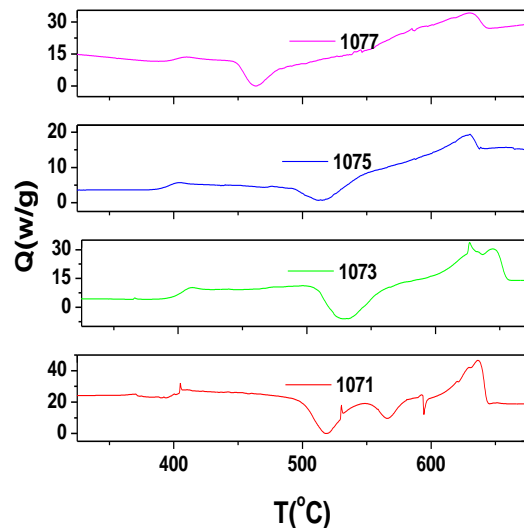


Fig7: DSC plots for bismuth boroaluminosilicate glasses

#### 4. CONCLUSIONS

A combination of thermal and spectroscopic measurements on bismuth borate glasses doped with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  glasses gives extraordinary results. The addition of  $\text{SiO}_2$  gives rise to density values which means packing of molecules become denser with addition of  $\text{SiO}_2$  diborate groups are formed. Formation of diborate groups is important feature of these glasses. Also the thermal stability against crystallization increases with the increasing content of  $\text{SiO}_2$  in bismuth borate and bismuth borosilicate glasses.

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