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Structural and Thermal Properties of B_2O_3-Bi_2O_3-CaO Glasses

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ABSTRACT

Glasses with compositions: $60B_2O_3$-(40-x) Bi_2O_3-xCaO (where x= 0, 5, 10, 15 and 20 mol%) have been prepared using melt quench technique. The density and molar volume have been determined. It is found that the density and molar volume decrease with increasing CaO content. The effect of Bi_2O_3 and CaO content on thermal stability, structure of the glass is systematically investigated by X-ray diffraction, SEM, infrared spectroscopy and DTA techniques. The glass transition temperature (T_g) of the samples was found to decrease with increase CaO content. IR measurements revealed an existence of trigonal BO_3 pyramid, tetrahedral BO_4 and BiO_6 octahedral structural units in the network of the investigated glass, Further, it confirm the conversation of four fold borate BO_4 to BO_3 groups, content which means that Bi_2O_3 and CaO plays the role of network modifier in the structural network.

1. Introduction

Glasses based on heavy metal and rare earth oxides have attracted considerable interests for their potential applications. Bi_2O_3 containing glass possesses higher refractive index, and exhibits high optical basicity, large polarizability and large nonlinear optical susceptibility [1]. In borate glasses, B_2O_3 is a best glass former because of its higher bond strength, lower cation size, smaller heat of fusion and valence of B_2O_3 can be considered as having the highest glass formation tendency because molten B_2O_3 does not crystalline by itself even when cooled at a slowest rate. The size of B^{3+} ion is very small and it can fit into the trigonal void created by three oxide ions in mutual contact, forming a BO_3 units. And there are the primary building blocks in all borate glasses. The physical properties along with structural properties of borate glasses can often be altered by the addition of a network modifier to the basic constituents [2-5].

Bi_2O_3 had recently been attractive materials of research due to their interesting physical properties leading to many applications [6]. These glasses find wide applications in the field of glass ceramics, layers for optoelectronic devices, thermal and mechanical sensors, reflecting windows, etc. Infrared spectroscopy and differential thermal analysis have also been used as important tools to study the nature of glasses for the past many years [7-9]. FT-IR spectroscopy becomes effective tools for resolving the structure of local arrangement in glasses [10-12] and it has been used since a long time to investigate the structure of different glasses [13].

Nam Tin Kim, et al. [14] have analysed the physical, thermal and optical properties of the B_2O_3-Bi_2O_3-ZnO glass system, in order to understand the effects of zinc oxide. The variation in the density and the molar volume with the ZnO content indicates that the effect of ZnO on the glass structure is dependent on its concentration and they observed that increasing the ZnO concentration results in a progressive increase in the number of non-bridging oxygens which in turn decreases the number of bridging oxygens.

Many investigations have been reported on ternary borate, bismuthate, calcium oxide glasses. To best of our knowledge, there are no reported on borobismuthate glasses mixed with calcium oxide. The aim of the present work is to investigate the $60B_2O_3$-(40-x)Bi_2O_3-xCaO (where x= 0, 5, 10, 15 and 20 mol%) glasses by measuring the physical, structural and thermal properties which include density and molar volume, XRD, SEM, FTIR and thermal analysis.

2. Experimental Methods

2.1 Glass Preparation

$60B_2O_3$-(40-x) Bi_2O_3-xCaO (where x= 0, 5, 10, 15 and 20 mol% composition were prepared. The Analytical reagent grade powders of boron trioxide (B_2O_3), bismuth oxide (Bi_2O_3) and calcium oxide (CaO) were mixed in the appropriate composition. The powders were mixed thoroughly and then melted in a silica crucible for 3 hours in muffle furnace at 1040 °C. The melt was poured into a brass mould to form samples of dimensions 10mm diameters and 6mm thickness. Glass samples were annealed at 375 °C for 2 hours to avoid the mechanical strain developed during the quench process. Then the furnace was switched off and glass was allowed to cool gradually to room temperature. The nominal compositions, density and molar volume of the prepared glasses is given in Table 1.

Table 1 Nominal compositions (mol.%), density and molar volume of glasses

Samples	Nominal Composition			Density (ρ)	Molar volume
	B_2O_3	Bi_2O_3	CaO	(x10^{-3} kg/m^3)	(V_m) cm^3/mol
BB	60	40	0	5.8560	38.96
BBC05	60	35	5	5.8311	35.61
BBC10	60	30	10	5.6458	33.15
BBC15	60	25	15	5.4214	30.74
BBC20	60	20	20	4.9587	29.48

2.2 Characterization

The amorphous nature of the sample is confirmed by X-ray diffraction technique using GE-Inspection technology 3003TT model made in Germany copper target operating voltage 40 Kv 300 mA current rate. The scanning electron microscopy (SEM) investigations were performed on glass samples at room temperature using a JEOL auto fine coater Model JES-1600 for morphological studies. The infrared spectra of the prepared glasses were obtained by KBr pellet technique in the wavenumber range 4000 - 400 cm^{-1} using AVATAR 330 series. Thermal studies were carried out in a STA - 1500 simultaneous thermal analyser instrument. Densities of the glasses were measured by the Archimedes method using deionised water as an immersion liquid. The accuracy of the determined densities of the different glasses is ±0.001 g/m^3.

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3. Results and Discussion

3.1 Density

The density is a powerful tool for exploring the changes in the structure of glasses. The density is affected by the structural softening/compactness, change in geometrical configuration, coordination number, cross-link density and dimension of interstitial spaces of the glass. The variation of density and molar volume is shown in Table 1. Thus decrease of a heavy metal ion leads to a decrease in the density that has a linear dependence on the composition. In the present glass samples density decrease linearly from 5.8560×10^{-3} kgm^{-3} to 4.9587×10^{-3} kgm^{-3} congruent with a linear decrease in the molar volume from 38.96 cm^3/mol to 29.48 cm^3/mol as the alkaline earth modifier is added at the expense of Bi_2O_3 content. The decrease in molar volume can be explained that molar volume depends on both, i.e. density and molecular weight and in the present glass system both decreases with the increase in CaO content at the expense of Bi_2O_3 content. Sujata Sanghi, et al. [15] studied the ternary glass system Fe_2O_3-CaO-Bi_2O_3 and found that the addition of CaO to the glass network the density and molar volume linearly decreases.

3.2 XRD and SEM Studies

Figs. 1 and 2 presents the XRD pattern of the sample containing 45% B_2O_3 which is typical for other samples. XRD patterns of all the as-prepared samples show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument. All the prepared glass samples are glassy nature (Fig. 1). The SEM microphotographs of BB and BBC20 glasses are given in Fig.3. These images clearly indicate that there is no crystalline phase existing in the overall surface of the samples. This further confirms the amorphous nature of the glass samples.

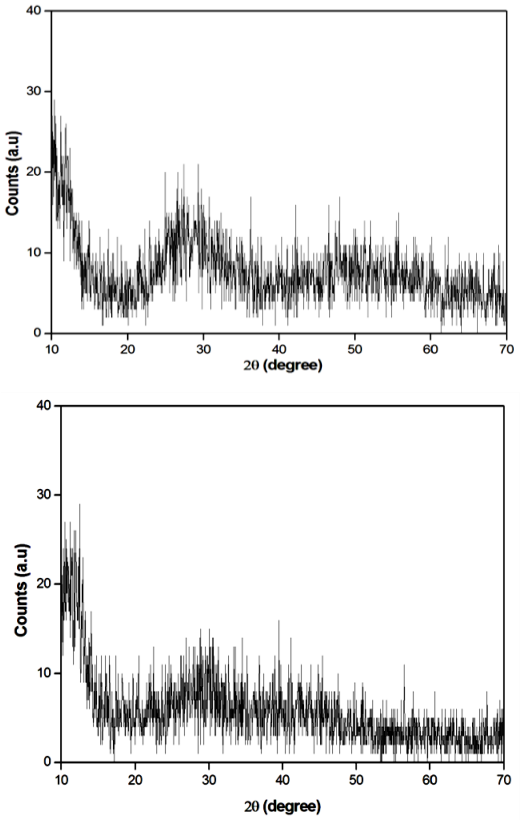

Fig. 1 X-ray diffractogram of BB(a) and BBC20(b) glass

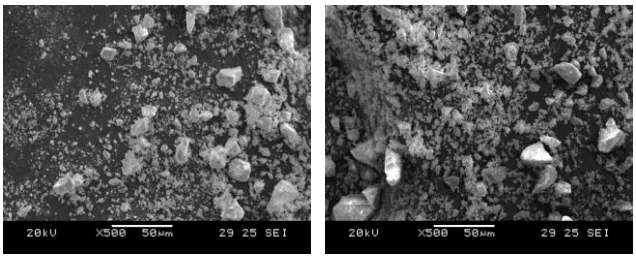

Fig. 2 SEM image of $60B_2O_3$-$40Bi_2O_3$ (a) and $60B_2O_3$-$20Bi_2O_3$-20CaO (b).

3.3 FTIR Study

The infrared spectra of $60B_2O_3$-(40-x) Bi_2O_3-xCaO glasses are recorded at room temperature in the frequency range between 4000 and 400 cm^{-1} as shown in Fig. 3. The observed bands along with their vibrational assignments of samples have been tabulated in Table. 2. The obtained broad bands may confirm the amorphous nature of the studied glass samples and are in agreement with XRD.

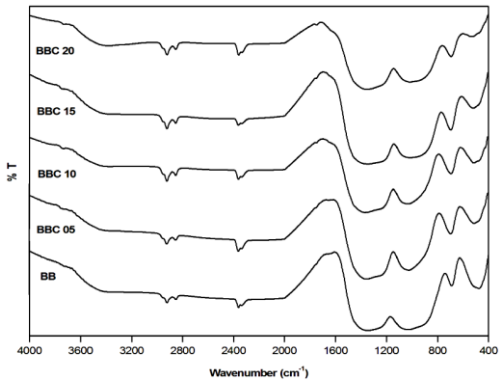

Fig. 3 FTIR spectra of BBC glasses with different concentrations of CaO

Table 2 Band positions and their corresponding assignments of infrared spectra of BBC glass systems

Wavenumber (cm^{-1})	Assignment	Ref.
~1334	B-O stretching vibrations of the trigonal BO_3 units	[17]
~1026	B-O stretching vibrations of BO_4 tetrahedral	[16]
~700	Bending vibrations of B-O-B linkage	[16]
~520	Bi-O bonds in BiO_6 units.	[17]
~480	Ca–O bending vibrations in the CaO units	[20]

The vibrational modes of the borate glass network show the presence of three infrared spectral regions. The first group of bands in the region 1200-1600 cm^{-1}, is due to the asymmetric stretching vibration of the B-O bond of the triangle BO_3 unit containing non-bridging oxygen ions. The second group lies between 800 and 1200 cm^{-1} and is due to the B-O bonds stretching of the tetrahedral BO_4 units. The third group is around 700 cm^{-1} and is due to bridging B-O-B linkages in the borate network.

The observed bands around at 700 cm^{-1} is due to the bending vibration of B-O-B [16] whereas the band at 1026 cm^{-1} is due to asymmetric stretching vibrations of the B-O bonds in BO_4 units [17] and the broad band at 1334 cm^{-1} is attributed to the B-O bonds due to stretching vibrations of trigonal BO_3 units in the borate network [18]**.** Also it is observed that a frequency region extends from 400 to 600 cm^{-1} assigned to Bi-O bonds in [BiO_6] octahedral units. Similar observation was found by Yasser B. Saddeek, et al. [19] in bismuth borate glasses. The [BiO_3] polyhedral vibration band at 840 cm^{-1} does not appear in the IR spectra, it can be concluded that only [BiO_6] octahedral units will be expected to influence the borate network of the investigated glasses [20]. The bands are located ~480 cm^{-1} which is due to the Ca–O bending vibrations in the CaO units [21].

As it is seen from Fig. 3, the spectrum of a binary $60B_2O_3$-$40Bi_2O_3$ glass contains BO_3, BO_4 and BiO_6 units. The addition of CaO at the expense of Bi_2O_3, the band at 1334 cm^{-1} shifts towards higher wavenumber. Also its intensity increases with the increase in content of modifier oxide, which is due to the formation of BO_3 units at the expense of BO_4 units. As further increase in the CaO content causes a weakening of the borate network. The stretching vibration of the B-O bonds in BO_4 units is shifts towards lower wavenumber with increase of CaO content. This behaviour can be explained that the BO_4 units will be destroyed and is converted into BO_3 units with NBOs.

The present IR spectra showed non-existence of band at 806 cm^{-1}, which reveals the absence of boroxol rings in glasses and hence it consists of only BO_3, BO_4 and BiO_6 groups [22, 23]**.** The broad band extending from 2300 to 3600 cm^{-1} is attributed to hydroxyl groups or water molecules.

3.4 Thermal Behaviour of BB and BBC20 Glasses

(i) BB and BBC20 Glasses

The T_g is strictly related to the density of cross–linking, the tightness of the network formers and the coordination numbers of the network forming atoms. The DTA curve for the BB glass shows a small endothermic hump corresponding to the glass transition temperature at 340 °C and this is followed by an exothermic peak corresponding to the crystallization temperature at 690 °C and the second endothermic peak corresponding to the melting temperature at 900 °C as shown in Fig. 4.

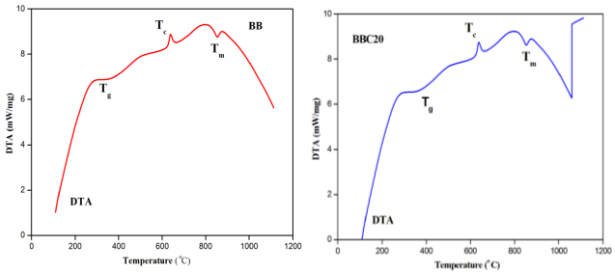

Fig. 4 DTA cure of BB and BBC 20 glass systems

Fig. 4. shows the differential thermal analysis curve for BBC20 glass. From the figure, it is observed that the first endothermic hump appear in the region 328 °C followed by exothermic peak at 663 °C and a second endothermic peak appears at 877 °C. Each peak is attributed to the glass transition temperature, crystallization temperature and melting temperature respectively. Addition of CaO into B_2O_3-Bi_2O_3 glass will change the borate structure by creating BO_3 units at the expense of BO_4 units.

Table 3 Values of glass transition temperature, crystallization temperature, melting temperature, thermal stability and Hruby's parameter of various glass samples

Name of the sample	Glass composition in mol%	Glass transition temp. (◦C)	Crystallization temp. (◦C)	Melting temp. (◦C)	Thermal stability (S)	Hruby's parameter (Kg1)
BB	60-40	340	690	900	350	0.625
BBC20	60-20-20	328	663	877	335	0.610

It is believed that T_g is depends on the strength of chemical bonds in the structure. CaO, play the role of a network modifier and non-bridging oxygen increases with the introduction of modifier content in the B_2O_3-Bi_2O_3 glass. Increase of non-bridging oxygen indicates the breaking of chemical bonds, which in turn decrease the T_g [24]. According to Yasser B. Saddeek and Gaafar [25], the decrease in value of T_g with the addition of Bi_2O_3 and Nb_2O_5 content indicates the formation of BO_3 units with non-bridging oxygen atoms.

Generally, the difference between crystallization temperature and transition temperature, gives a measure of stability of a super cooled liquid (glass) i.e. stability factor S. The larger value of S, gives the better thermal stability of super cooled liquid [26]**.** Table 3 shows the values of T_g, T_c, T_m, glass stability factor (S) and Hruby's parameter (K_{gl}). Hruby's parameter gives the information on the stability of the glass against devitrification. From the table, it is observed that the glass stability factor and Hruby's parameter of the BB glass sample are high compared with BBC glasses. The stability of the glasses is in the order of BB > BBC.

4. Conclusion

The conclusions drawn from these studies for BB and BBC glass system are summarized as: The density as well as molar volume of the BBC glasses decreases with the increase in CaO content. This is due to the difference in the atomic masses of Bi_2O_3 and CaO ions. X-Ray diffraction pattern shows the amorphous behaviour of the prepared samples. FT-IR confirmed the existence of trigonal and tetrahedral borate groups with an establishment of Bi-O bonds in [BiO_6] units. The thermal stability of the investigated glass systems decreases with the addition of CaO content. The stability of the glasses is in the order of BB > BBC. The topographical aspects of the glass samples are reported from SEM micrograph.

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