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RESEARCH ARTICLE

STRUCTURAL AND THERMAL PROPERTIES OF $B_2O_3+K_2O+B_AO$ GLASSES

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ABSTRACT

A series of glasses were prepared by melt quench technique in the glass system $60B_2O_3$-(40-x)K_2O-xBaO (where x=0, 5, 10, 15 and 20 mol%).The structural and thermal properties were studied using FTIR and DTA techniques. IR results show that glass network consists of BO_3 and BO_4structural groups and the BO_4 increases with increasing BaO content. Thermal stability of the investigated glasses increases with the addition of BaO content at the expence of K_2O.The properties of glasses were discussed in terms of the relative proportion of modifier oxide.

INTRODUCTION

Borate glasses are one of the important categories of glasses, having interesting structural peculiarity and they are known today as important material for insulation (glass wool) and textile (continuous filament) fiber glass. Therefore, precise knowledge of the structure and properties of B_2O_3 – based glasses and melts is increasingly required from both fundamental and industrial points of view. The insulating property of borate glasses turns into a semiconducting or electronic or ion conducting nature, when metal oxides such as alkali and alkaline earth oxides are added to them. Alkali borate glass systems are good candidates for ion conduction and suitable for the fabrication of solid state batteries [1,2].

B_2O_3 is a basic glass former because of its higher bond strength, lower cation size, smaller heat of fusion and valence (3) of B. It 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, BO_3 units are a primary building blocks in all borate glasses [3]. The properties of borate glasses can be modified either by changing their composition or by adding different additives like alkali/alkaline earth oxides which leads to the structural changes in borate glasses [4-6].

The aim of this paper is to prepare the borate based (B_2O_3-K_2O-BaO) glasses and their properties was investigated using FTIR and thermal studies. In general, barium ion has large radius and strong polarizing power, incorporating Ba^{2+} ions to the glass system may improve dramatically the glass forming ability. The study of structural and thermal properties of alkali /alkaline earth oxide doped borate glasses inspired many researchers [7-9].

Experimental Procedure

Glass preparation

A series of glass samples of formula$60B_2O_3$- *(40-x)* K_2O *– xBaO* with x varying from 0 to 20 mol% composition were prepared by using the melt quench technique. The raw materials of boron trioxide (B_2O_3), potassium oxide (K_2O) and barium oxide (BaO) were mixed together by grinding to obtain a fine powder. The obtained mixture was melted in a silica crucible for three hours in a muffle furnace at temperature of 800 – 900°C until a bubble free liquid is formed. The melt was poured into a brass mould to form samples of dimensions 10 mm diameters and 6mm thickness. Glass samples were annealed at 350 ºC for 2 hours to avoid the mechanical strain developed during the quench process. Then the oven was switched off and glass was allowed to cool gradually to room temperature. Diamond disc and diamond powder were usedto smoothen the prepared glass samples and to keep their

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surfaces perfectly plain. The nominal composition of glass samples is listed in Table1.

Infrared spectra of the powdered glass samples were recorded at room temperature in the wavelength range4000 - 400 cm^{-1} using a SHIMADZU 8400 FT-IR spectrometer. These measurements were performed on glass powder dispersed in KBr pellets. Differential thermal analyses (DTA) have been carried out using SDT-Q600 version 8.0 instruments at a heating rate of 20°C/min in nitrogen gas atmosphere.

RESULTS AND DISCUSSION

The IR spectra of $60B_2O_3$ $(40-x)K_2O$-xBaO (where x = 0, 5, 10, 15 and 20 mol%) glasses were recorded at 303 K in the frequency range between 4000 and 400 cm^{-1} as shown in Fig. 1. The spectra occur due to change in the dipole moment of the molecule. It involves the twisting, bending, rotating and vibrational motions in a molecule. The obtained absorption bands and their assignments are summarized in Table 2.

Table.1 Nomenclature and the composition of glass samples

Nomenclature	Composition (mol %)		
	B_2O_3	K_2O	BaO
BKBa 05	60	35	5
BKBa 10	60	30	10
BKBa 15	60	25	15
BKBa 20	60	20	20

Table 2 Band positions and their corresponding assignments of infrared spectra of BKBa glasses

Wave number cm^{-1}	Assignments
~ 1392	B-O stretching vibrations of BO_3 units in metaborate, pyroborate and orthoborate groups.
~927	B-O stretching vibration of BO_4 units in tri- tetra and penta borates groups.
~ 719	Bending vibrations of B-O-B linkage.
~ 451	Specific vibrations of metal cation such Ba^{2+}.

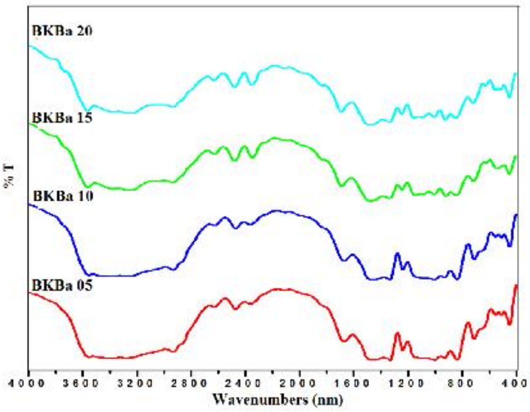

Fig.1 Infrared spectra of BKBa glasses with different concentration of BaO

The vibrational modes of the borate network are mainly active in three IR spectral regions (i) 1200-1400 cm^{-1}; (ii) 800-1200 $cm^{-1}$and (iii) 400-800 cm^{-1}. The first region is attributed to the stretching and relaxation of the B-O bond of the trigonal BO_3 units, while the second region is attributed to BO_4 units and the third one is due to the bending of B-O-B linkages in the borate network. The FTIR spectra of the glass samples exhibit similar features as reported in various literature [10, 11].

Fig. 1shows some peaks around 1392, 927, 719 and a shoulder around 451 cm^{-1}. The well-known characteristic band (at 806 cm^{-1}) of vitreous B_2O_3 is assigned to the symmetric stretching vibrations of the boroxol rings. The peak at 806 cm^{-1} is found missing in the IR spectra of glasses which indicates the absence of boroxol ring in the glass network.

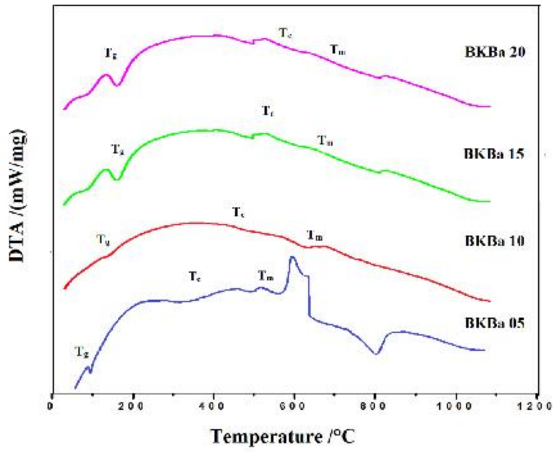

Fig.2 Differential thermal analysis curves for BKBa glass sample

In the studied glasses, the band at 1392 cm^{-1} is due to the asymmetric stretching vibrations of trigonal BO_3 units [12] in meta- pyro- and orthoborate units and a band at 927 cm^{-1} is due to B-O bond stretching of BO_4 groups [13].The addition of alkaline earth ion at the expense of K_2O into the glass matrix increases in the intensity of band due to BO_4 and decreases in the intensity of the band due to BO_3structural units, indicating a gradual increase in the formation of BO_4 units with bridging oxygen atoms. Also, its intensity increases with the increase in the percentage of BaO, which is due to the conversion of trigonal BO_3 to tetrahedral BO_4 groups and increase in tetrahedral BO_4 groups in the borate network.

Table 3 Values of glass transition temperature (T_g), crystallization temperature (T_c),melting temperature (T_m), thermal stability (S) and Hruby's parameter (K_{gl}) of BKBa glasses

Name of the glass	Glass transition temperature T_g/°C	Crystallization temperature T_c/°C	Melting temperature T_m/°C	Thermal stability (S)	Hruby's parameter (K_{gl})
BKBa 05	105	332	522	227	1.19
BKBa 10	129	460	632	331	1.92
BKBa 15	156	520	630	364	3.30
BKBa 20	160	574	662	414	4.70

In all the IR spectra, a band appears around 719 $cm^{-1}$is assigned to the bending vibrations of BO_3 groups [14]. The band around 451$cm^{-1}$are assigned to specific vibrations of metal cations Ba^{2+} [15]. Barium oxide will act as glass modifier and convert the BO_3 triangles into BO_4 groups.

Thermal analysis

Fig 2 shows the differential thermal analysis curves for borate based glasses. The DTA exhibitsa small endothermic hump at lower temperature in the glass samples, which is characteristic of glass transition temperature (T_g) region followed by a exothermic peak and is characteristic of crystallization temperature (T_c). The exothermic followed by a endothermic peak, which is characteristic of a melting temperature (T_m).The value of T_g, T_c and T_m increases from 105 to160℃, 332 to 574℃ and 522 to 662℃ with an increasing BaO content respectively. The results indicate that increase in BaO concentration increases the rigidity of the glass network.

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. Table 3shows 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 increase with increasing BaO content. This is due to the formation of BO_4 groups at the expence of BO_3 groups and increasing stability factor confirms the increasing in rigidity of the glass structure [16].

CONCLUSION

In this work, we have studied the structure and thermal properties of the ternary B_2O_3-K_2O-BaO glasses. The FTIR measurements indicate the presence of the BO_3 and BO_4 units in the glass structure and its dependence on the BaO content. Thermal stability of the investigated glass system increases with the addition of BaO content at the expense of K_2O.

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