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RESEARCH ARTICLE

THERMAL STABILITY AND FT-IR STUDIES OF B_2O_3+K_2O+MgO GLASSES

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ABSTRACT

B_2O_3-K_2O-MgO glasses with different concentrations of MgO (0-20 mol. % in the steps of 5) were prepared by melt quench technique. Structural characterizations of these glasses were conducted through FT-IR, DTA and density measurements. The amorphous nature of the glasses was checked by X-ray diffractometry (XRD). The transformation of BO_3 trigonals to BO_4 tetrahedral units has evidenced from the FT-IR spectra of the prepared glass samples and the BO_4 units increases with an increasing concentration of MgO content. The transition temperature (T_g), melting temperature(T_m) and crystallization temperature (T_c) have been identified using DTA measurements. The transition temperature (T_g) increases with an increase of MgO content. Density of the glasses increases whereas molar volume decreases which reveals the compactness of the glasses. The structural properties of these glasses were discussed in terms of the relative proportion of potassium and magnesium oxides.

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INTRODUCTION

Alkali borate glasses constitute interesting system because of several structural changes induced upon the concentrations of alkali oxide to the B_2O_3 glasses. Fused B_2O_3 is assumed to consist of boroxyl rings and BO_3 triangles and constitutes a random network composed of two dimensional units. The existent of several structural groups consisting both three and four coordinated borons (e.g. pentaborate, tetraborate, triborate and diborate groups) was first postulated by Krogh –Moe (Krogh-Moe, 1969) and confirmed by comparison with IR spectra of crystalline sodium borate compounds. It was found that at high alkali contents, the fraction of BO_4 units decreases and non-bridging oxygens (bounded only to a single boron atom) become the dominant one in the glass (Mohan *et al*., 2008). The addition of alkaline oxide to alkali borate glasses have been studied extensively by several researchers (Kamitsos and Karakassides, 1989 and Kamitsos *et al*., 1989). Alkaline earth oxides MgO, CaO, SrO, BaO improve glass forming ability. These oxides at low concentrations act as glass network formers (GNF) and at higher concentrations behave as glass network modifiers (GNM) (Gabr *et al*., 2007). Alkali / Alkaline - earthoxy borate glasses find variety of applications in solid – state batteries, phosphors, solar energy converters, optical devices and in a number of electronic devices (Sanghi *et al*., 2004). These glasses are relatively high moisture-resistant, possess high mechanical strength when compared with the pure borate glasses (Balaji Rao *et al*., 2004). In this article, the physical and structural properties of $60B_2O_3$ - *(40-x) K_2O – x MgO (where x=0, 5, 10, 15and 20 mol %)* glasses are discussed with the help of density, FT-IR and thermal measurements.

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Experimental Procedure

Glass Preparation

Alkaline earth borate glasses $60B_2O_3$ - *(40-x) K_2O – x MgO were* prepared by melt quench technique. In current glass system, a gradually increase in the concentration of MgO was done from 0 to 20 mol% while K_2O concentration was decreased from 35 to 20 mol%. The Analytical Reagent grade powders of boron trioxide (B_2O_3), potassium oxide (K_2O) and magnesium oxide (MgO) of appropriate proportion were grind in an agate mortar thoroughly for 60 minutes to form a homogeneous mixture and then melted in a crucible for 3 hours in a muffle furnace at 900℃. The melt was poured into a brass mould to form samples of dimensions 10mm diameter and 6mm thickness. To avoid the mechanical strain developed during the quench process, the glass samples were annealed at 450 ºC for 2 hours. Then the furnace was switched off and the glasses were allowed to cool gradually to room temperature. Diamond disc and diamond powder were used to smoothen the prepared glass samples and to keep their surfaces perfectly plain.

Ccharacterization

The amorphous nature of glasses were determined by X-ray diffraction technique using GE-Inspection technology 3003TT model made in Germany, copper target at operating voltage 40 Kv and 300 mA current rates. The prepared glass samples were grind with potassium bromide (KBr) pellet techniques operated between wave number ranges from 400 to 4000 cm^{-1} and the infrared absorption spectra is obtained using FTIR Spectrometer. The Differential ThermoGravimetric Analysis (TG-DTA) was carried out on a SETARAM Labsys, TM TG-DTA16 thermal analyzer between 100–1200K temperature range at heating rate of 10 °C min^{-1}. The densities of samples were calculated using Archimedes standard principle of using water as a buoyant liquid. The nomenclature and the composition in mol% of different glasses are given in Table 1.

Table 1. Nomenclature and the composition of glass samples

Nomenclature	Composition (Mol %)		
	B_2O_3	K_2O	MgO
BKM05	60	35	5
BKM10	60	30	10
BKM15	60	25	15
BKM20	60	20	20

RESULTS AND DISCUSSION

X-ray diffraction

The XRD pattern of BKM05 and BKM20 glasses is shown in Fig.1. The patterns exhibit no sharp peaks from which the amorphous nature of the glass samples is confirmed (Singh *et al*., 2011; Reduan *et al*., 2015 and Maqableh *et al*., 2014). The entire prepared glass samples are glassy nature.

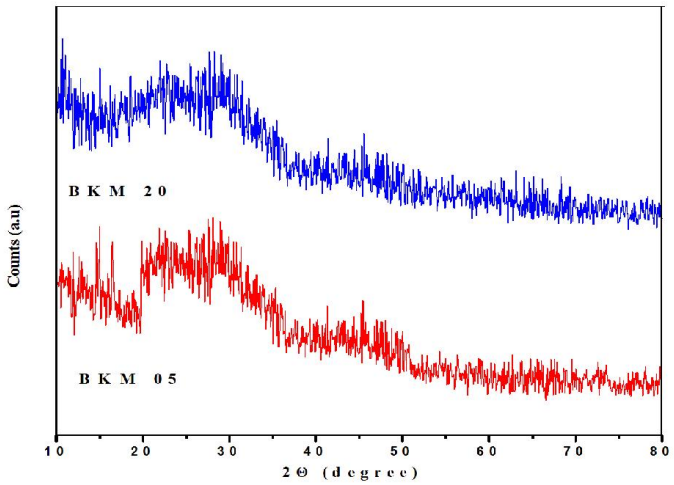

Fig. 1. XRD patterns of BKM 05 and BKM 20 glasses

Density and molar volume

The values of density and molar volume of the different glass samples with respect to change in mol% of MgO are listed in Table 2. The density of the glass network depend upon many factors such as structure, coordination number, cross-link density and dimensionality of interstitial space (Khor *et al*., 2012). The density increases with an increasing MgO content. A reverse trend is observed for molar volume (Magdalena Szumera, 2014 and Agnesi *et al*., 2009). The addition of MgO into the B_2O_3-K_2O glass causes the density to increase and this indicates that the MgO altered the structure of glass by converting BO_3 units into BO_4 units in the network, so the structure turns out to be more compact. Further, increase of MgO content at the expense of K_2O causes the increase in density values and consequently the increase in BO_4 groups. The molar volume (V_m) is of greater interest, since it relates directly to the spatial distribution of the oxygen in the glass network. The table reveals that V_m decreases with increasing MgO content. This could be explained by considerable formation of bridging oxygen (Chethana *et al*., 2012).

FT-IR Spectroscopy

The infrared spectra of $60B_2O_3$- (40-x) K_2O - xMgO glasses are recorded at 303K in the frequency range between 400 and 4000 cm^{-1} as shown in Fig.2. The observed bands along with their vibrational assignments of samples have been tabulated in Table 3. The obtained broad bands confirm the amorphous nature of the studied glass samples and are in good agreement with XRD.

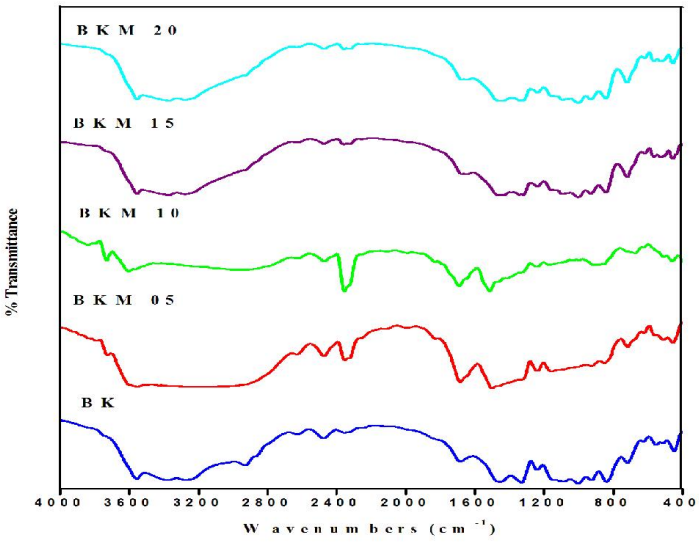

Fig. 2. Infrared spectra of BKM glasses with different concentration of MgO

Table 2. Summary of data on various physical parameters of B_2O_3-K_2O-MgO glasses

Name of the Glass	Density (ρ) × 10^{-3} kgm^{-3}	Molar volume (V_m) cm^3/mol	Oxygen packing density(O)	Average molecular weight (M)	Total Magnesium ion concentration N_i (cm^{-3})	Inter-ionic distance of Mg ions R_i (Å)
BKM05	2.340	39.38	5.585	92.160	0.764	1.093
BKM 10	2.473	35.28	6.234	87.265	1.706	0.836
BKM 15	2.526	32.60	6.746	82.369	2.770	0.712
BKM 20	2.619	29.58	7.437	77.474	4.072	0.626

Table 3. Band positions and their corresponding assignments of infrared spectra of BKM glass system

Wave number (cm^{-1})	Assignments
~ 1342	B-O asymmetric stretching vibration of the trigonal BO_3^- units.
~ 1006	B-O stretching vibration of BO_4 tetrahedral.
~925	MgO_4 tetrahedral.
~ 717	Bending vibration of B-O-B linkage.
~ 453	Specific vibrations of Mg^{2+} Ions.

and BKM4 glasses. The T_g is strictly related to the density of cross-linking, the tightness of the network formers and coordination numbers of the network forming atoms. The T_g, T_m and T_c values increase from 144°C to 159°C, 456°C to 531°C, 634°C to 690°C with the introduction of MgO content at the expense of K_2O content. Further, increase in percentage of MgO content modifies the glass structure and the values of T_g, T_m and T_c increase with increase of MgO content. This is due to the decrease in the number of non-bridging oxygens and consequently the increase in connectivity of the glass network

Table 4. 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 BKM glass system

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})
BKM 05	144	456	634	312	1.75
BKM 10	159	531	690	372	2.33
BKM 15	162	628	722	466	4.95
BKM 20	165	641	728	476	5.47

The band positions are assigned with different structural units according to various authors (Verhoef *et al*., 1992; Ram, 1995; Bobkova and Khot'ko, 2005 and Doweidar *et al*., 2013). The bands around 1200 -1400 cm^{-1} arises due to the asymmetric vibrations of the B – O bond of trigonal BO_3 units containing non- bridging oxygen ion. The bands in the range 800-1200 cm^{-1} are due to stretching vibrations of the B –O bonds in BO_4 units. The band around 700 cm^{-1} is assigned to the bending vibrations of the B-O-B linkage. In the alkaline earth borate glasses, the band at 1342 cm^{-1} is due to to B-O asymmetric stretching vibrations of BO_3 units (Chekhovskii and Fisika Khimiya Stekla, 1985).

The peak shifted from higher to lower wave numbers with the addition of MgO to B_2O_3-K_2O glass matrix. This may be due to increase in bond length of B-O groups and formation of BO_4 units. Similar conclusion was also reported by Ramadevuda *et al*. (2011). The stretching vibration of tetrahedral BO_4 units (at 1006 cm^{-1}) is shifted to higher intensity with increasing MgO content. This is due to the formation of BO_4 units at the expense of BO_3 units. The bands of arte located at around 925 cm^{-1} which is due to MgO_4 tetrahedra (Kamitsos *et al*., 1990). Another band is also observed around 717 cm^{-1} due to the bending vibration of B-O-B linkages in the borate glasses. The band at 453 cm^{-1} shows the existence of vibration of Mg^{2+} ions in the network vacancies (Ramadevudu *et al*., 2012). In common, the absorption band at 806 cm^{-1} is accredited to the boroxol ring in the borate glass network. In the present study, the absence of peak at 806 cm^{-1}, indicates the absence of boroxol ring in the glass network due to conversion of BO_3 triangles into BO_4 tetrahedral (Venkateswarlu *et al*., 2014). The addition of MgO into BK glass matrix, there is a clear increase in the BO_4 units and decrease in the BO_3 structural units, indicating a increase in the compactness in the glass network.

Thermal analysis

Table 4 gives the transition temperature (T_g), melting temperature (T_m) and crystalline temperature (T_c), Thermal stability and Hruby's parameter for BKM1, BKM2, BKM3 (Larsen, 1998; Li *et al*., 2013 and Ji-fang *et al*., 2012). In general, the difference between crystallization temperature and transition temperature, gives a measure of stability of a super cooled liquid which is stability factor (S). Larger the stability factor, better is the thermal stability of the super cooled liquid. Hruby's parameter (K_{gl}) gives the information on the stability of the glass against devitrification. From the table 4, it is observed that the S and K_{gl} increase with increasing MgO content (Abdel-Rahim *et al*., 2008 and Reduan *et al*., 2014). The increase in the values of the S and K_{gl} has been attributed to an increase in the packing density and rigidity and hence the formation of stronger structural building units in the glass network. Thereby indicating that the incorporation of MgO helps to form more tightly packed glasses.

Conclusion

In summary, it is concluded that the glass samples of composition $60B_2O_3$ - (40-x) K_2O - xMgO (where x=0, 5, 10, 15 and 20 mol. %) has been successfully developed which is transparent, moisture resistant and stable. From the XRD profiles, the amorphous nature of the glasses sample is confirmed. The density of the glass systems increases whereas molar volume decreases with increase in mol% of MgO, which in turn increases the connectivity of the network structure. The FT-IR spectral studies have indicated the transformation of BO_3 triangles to BO_4 tetrahedral for the glass samples with an increase in MgO content. Thermal stability of the investigated glasses increases with increasing MgO content at the expense of K_2O.

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