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Research Article

SPECTROSCOPIC CHARACTERIZATION OF STRONTIUM DOPED MANGANESE BORATE GLASSES

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ABSTRACT

The effect of increasing strontium content in the manganese borate glasses of composition xSrO - (40-x) MnO_2 - 60B_2O_3, prepared by the conventional melt quenching technique was studied. XRD confirms the amorphous nature of the samples. Thermal and spectroscopic behavior of the glass system was studied by DTA and FTIR analyses. FTIR reveals the presence of various functional groups present as well as the conversion of BO_3 to BO_4 units on the subsequent addition of modifier SrO. DTA gives an insight into the glass transition temperature, crystallization temperature, melting temperature and hence the stability of the glasses.

INTRODUCTION

B_2O_3 is a well known glass former possessing the ability to host metals and chemical stability (Roshan Lal *et al*, 2004), having unique properties like reduced thermal expansion, resistance to thermal shock, enhanced toughness, strength in chemical resistance and durability (M. S: Dahiya *et.al*, 2015). Because of the attractive properties, temperature, radiative relaxation and low melting point, borate glasses have become one of the most promising materials for advanced technology applications (M. Santiago *et al*, 1998; N. Can. T. Kanali *et al*, 2006). Addition of alkali, alkaline and transition metal oxides to borate glass matrix result in the glass network modification giving rise to desired properties, making suitable for appliances. B_2O_3 consists of boroxol rings (B_3O_6) and a few triangular borate units . By the addition of transition metal ions to the borate glasses, they would exhibit specific physical properties. When these glasses are grafted with alkaline earth ions, the resultant glasses are found to have several potential applications such as radiation dosimetry, phosphors, solar energy convertors, vacuum ultraviolet optics and semiconductor lithography and a number of electronic devices (W.L.konijendijk *et al*, 1975).

Among various transition metal ions, manganese ions have strong bearing on the optical, magnetic and electrical properties of glasses. A large number of interesting studies is available on the environment of manganese ions in various inorganic glass systems. The transition metal oxide such as manganese oxide is chosen in the present study as it exists in different valence states. MnO_2 exists in different valence states with different coordination in glass matrices. Study of manganese with different coordination with different valence states in the glass matrix depends upon the quantitative properties of the modifiers, glass formers, size of the ions in the glass structure.

The addition of small amounts of alkaline earth oxide introduces additional oxygen ions which convert BO_3 units to BO_4 units. This transformation bring about a fourth bridging boron oxygen bond per boron center causing the raise in glass transition temperature T_g and hence in the rigidity of glass (Y.Yiannopoulos *et al*, 2001). SrO is a modifier oxide which enters into the glass network by breaking up the random network. Usually, oxygen atoms of the alkaline earth oxides break the local symmetry, while the cations occupy the interstitial positions in the glass system. Sr^{2+} incorporation into glasses increase the hardness of bioactive glasses. Strontium ions depress bone resorption and maintain bone formation. Glass and glass-ceramic system of lead titanium borate containing different ratios of SrO are assumed to be promising for capacitor applications due to their high dielectric constant (J. Shankar *et al*, 2012).

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The study of spectroscopic and thermal properties can help to throw some light on the structural aspects of the glasses. Hence the investigation of the prepared glasses using FTIR and DTA analysis reveals the thermal changes taking place during preparation of glasses.

The present work focuses at understanding the influence of SrO on the structural, spectral and thermal characteristics of the manganese borate glasses through the studies of XRD, FTIR and DTA. This analysis provides useful information about the nature of local environment of strontium ions and neighboring ligands of the glass matrix.

Experimental Details

The glass samples of composition $60B_2O_3$-(40-x) MnO_2-xSrO (where x=2,4,6,8,10 mol%) were prepared by conventional melt quenching method using the required chemicals of reagent purity grade. The batches were mixed and ground into fine powder using a porcelain mortar and then melted by keeping in a porcelain crucible in a thermal cyclic furnace at 1100°c for 1 hr. The melt was removed from the furnace several times and shaked well to ensure homogeneity. Then the molten samples were quenched at room temperature by pouring into copper mould having dimensions of 10 mm diameter and 6 mm thickness and subsequently annealed for two hours to avoid any mechanical strain developed. The samples prepared were chemically stable and non- hygroscopic. Then they were polished and surfaces were made perfectly plane and smoothed by diamond disc and diamond powder. The nominal compositions of SMB glass samples are given in Table 1.

The XRD patterns of powdered glass samples are recorded by X ray diffraction technique using the G.E. Inspection Technology 300377 model made in Germany of copper target of operating voltage 40 kV, 300 mA. The FTIR transmitter spectra of the glasses in the 400-4000 cm^{-1} spectral range were obtained with a resolution of 4 cm^{-1} by FTIR spectrophotometer model Spectrum RXI, Perkin Elemer using the KBr pellet technique.

Structural and Thermal analysis techniques yield specific physical properties and verify some important transformations in materials of the glasses as a function of temperature. The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature T_m of these glasses were determined by differential thermal analyses traces, recorded using thermal analyzer NETZSCH-STA449FS JUPITER instrument at a heating rate of 20°C/min in nitrogen gas atmosphere.

The nomenclature and composition of the prepared glass system are given in Table 1

Table 1 Nomenclature and composition of SMB glass samples.

S. No.	Nomenclature	Composition in mol %	Remarks
	SrO - MnO_2 - B_2O_3	**SrO - MnO_2 - B_2O_3**	
1	SMB1	2 - 38 - 60	Mol % of B_2O_3 is constant
2	SMB2	4 -36 - 60	
3	SMB3	6 - 34 - 60	
4	SMB4	8 - 32 - 60	
5	SMB5	10 - 30 - 60	

RESULTS AND DISCUSSION

XRD Analysis

Fig 1 shows the XRD pattern of SMB1, SMB5 glasses respectively. It can be seen that there is no continuous or discrete sharp peaks that confirmed the amorphous and homogeneous nature of the all the prepared samples. The absence of long range atomic arrangement is an indication of glassy nature of the samples.

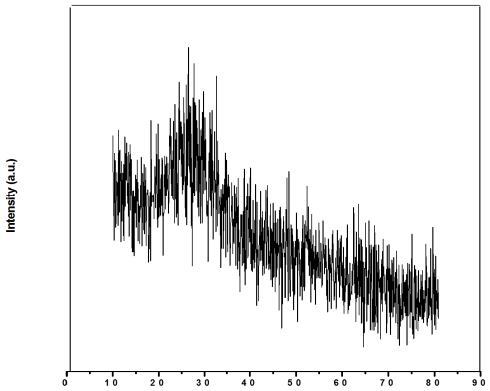

Figure 1 XRD pattern of SMB1 sample

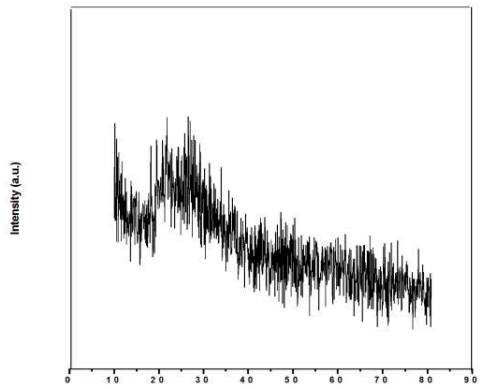

Figure 2 XRD pattern of SMB5 sample

Ftir Analysis

Infrared spectroscopy is an important tool for understanding the structure and dynamics of amorphous materials. The information regarding arrangements of network, structural units in the glasses can be obtained by studying the infrared spectroscopy as the absorption band vibrations are independent of vibrations due to other group of atoms (P. Pacutta *et al*, 2009; F. H. Elbatal *et al*, 2007). IR spectra may help to get the idea of nature of vibrations taking place in the disorder system which would be useful to get an insight to the system so as to Study the effect of alkaline earth ion on the borate network. It is also used to assign the observed absorption peaks to the proper vibration of the atoms in geometric grouping (Chandkiram gautam *et al*, 2013).

The FTIR spectra of the strontium doped manganese borate glasses is shown in Fig.3. In general, every IR analysis comprises of three distinct regions. The first two regions are assigned to stretching vibrations of tetrahedral BO_4 and trigonal BO_3 units i.e,

1. The region of 800-1200 cm^{-1} represents the stretching vibrations of B-O bonds in BO_4 units

2. The region extending from 1200-1600 cm^{-1} includes the vibrations of BO_3 units.
3. The third region lying between 600 to 800 cm^{-1} is due to bending vibration of various borate segments.

The observed band positions and their corresponding assignments of samples are tabulated in Table 2. The well known characteristic band of vitreous B_2O_3 is assigned to the symmetric stretching vibrations of boroxol rings. The replacement of MnO_2 by SrO breaks these rings and hence consists of only BO_3 and BO_4 units.

The broad bands of the spectrum confirm the amorphous nature of the samples (M.S. Gaafar *et al*, 2009; E.I. Kamitos *et al*, 1993). A weak band obtained around 2900 cm^{-1} is attributed to O-H vibrations of bond of water group. The broad band around 1396 cm^{-1} is due to stretching vibrations of B-O bond in BO_3 units (Y. Gandhi *et al*, 2009; Yasser. B. Sadeek *et al*, 2007). Intensity of this band decreases as SrO concentration increases. Band around 1027 cm^{-1} is assigned to stretching vibrations of B-O bond in BO_4 tetrahedral units (M.S. Gaafar *et al*, 2009). A band around 697 cm^{-1} stands for B-O-B bond bending vibrations of bridging atoms (E.I. Kamitsos *et al*, 1993). A band centered around 460 cm^{-1} represents the specific vibrations due to SrO. As the concentration of SrO increases, it is seen that the band of BO_3 groups get narrowing and shifted to lower wave numbers which implies that there is a considerable decrease in the number of non bridging oxygens. This is due to the modifying nature of SrO, the addition of which leads to the association of strontium atoms to boron and conversion of three coordinated borate units to four coordinated tetrahedral borate units. Hence the spectrum clearly depicts the impact of SrO doping on the manganese borate glass matrix transferring into a more polymerized network. This kind of behavior was also observed by T.Y.Lim *et al* (T.Y.Lim *et al*, 2014).

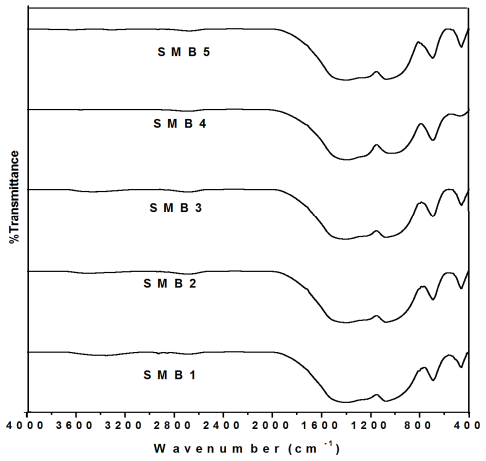

Figure 3 FTIR spectra of strontium manganese borate glasses

Table 2 Band positions and their corresponding assignment of IR spectra of all SMB glass compositions

Wavenumber (cm^{-1})	Assignment
460	Specific vibration of Sr-O
697	Bending vibration of B-O-B
1027	Stretching vibration of BO_4 tetrahedral
1396	B-O stretching vibration of trigonal BO_3
2900	O-H stretching vibration of water molecules

Thus the subsequent addition of SrO into the manganese borate glass system causes the transformation of BO_3 units into BO_4 units and decrease of non bridging oxygens resulting in a more strong, well connected closely packed glass structure.

Thermal Analysis

DTA analysis helps to understand the thermal behavior of the system indicating the structural changes occurring over the system as a function of temperature on the addition of modifier. DTA measurements capture the information regarding glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m). DTA traces for the prepared glass samples SMB1, SMB3, SMB5 are shown in the figure 3. In each DTA curve, there is a small endothermic peak, an exothermic peak followed by another endothermic peak. The first endothermic peak represents the glass transition temperature T_g, the exothermic peak indicates the crystallization temperature T_c while the second endothermic peak reveals the melting temperature T_m.

Thermal stability of the glass is an important property and the structure of the glass determines the thermal stability. According to Hruby, thermal stability is given by

$$H = T_c - T_g / T_m - T_c$$

For H <= 0.1, glass stability is poor but for H<= 0.5, it is superior (N. Soga *et al*, 1998).

The values of glass transition temperature (T_g), crystallization temperature (T_c) and the melting temperature (T_m) obtained from the DTA traces are given in Table.3.

The well separated peaks for T_g and T_c in the DTA traces confirm the high thermal stability of these glass samples. The incorporation of SrO into the glass matrix in small amounts increases the T_g which implies that the rigidity of the glass system increases as the SrO concentration increases. The glass transition temperature of borate glasses is linked with the atomic arrangements present in the glass system (M.A.Samee *et al*, 2011). The increase in glass transformation temperature implies the decrease in non bridging oxygen (S.Laila *et al*, 2014). Also increase in T_g may be attributed to increase in crosslink density and tightness of the packing of the glass network.

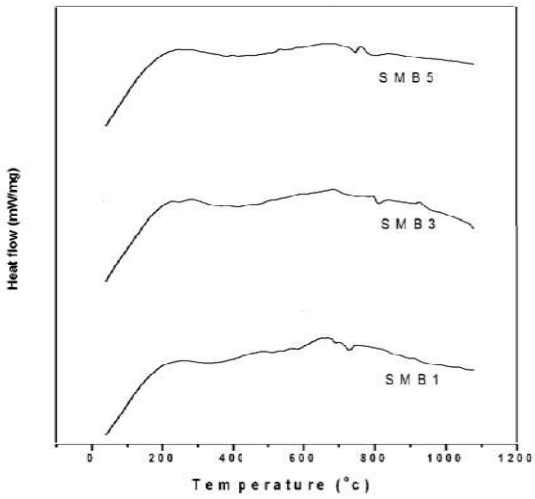

Figure 4 DTA traces for the strontium manganese borate glasses (SMB)

Table 3 Summary of DTA results

Sample	T_g (^{o} C)	T_c (^{o} C)	T_m (^{o} C)	Stability factor	Hruby's parameter
SMB1	359	637	755	278	2.3559
SMB3	368	684	805	316	2.6166
SMB5	386	705	814	319	2.9266

It is observed from the table that the values of T_g, T_C and T_m increase as the concentration of added mol% of SrO increases. T_g increases from 359^o C to 386 ^{o} C, Tc from 637 ^{o} C to 705 ^{o} C while Tm from 755 ^{o} C to 814 ^{o} C. The Hruby's parameter also increases from 2.355 to 2.9266 showing the increase in stability of the glasses due to the gradual addition of SrO. The increase in T_g is always attributed to increase in stability and network connectivity. This may be due to the higher bond strength of SrO (426.3) replacing MnO_2 (402.9) and formation of more covalent bonds. Thus the parent glass structure is turned into more stable, rigid structure by the added SrO content due to the conversion of more BO_3 into BO_4 units and higher bond strength.

CONCLUSION

The XRD study confirms the amorphous nature of the glass samples. FTIR spectra reveals the presence of both trigonal BO_3 and tetrahedral BO_4 groups and incorporation of SrO is found to affect the glass structure by converting trigonal BO_3 into tetragonal denser BO_4 units. Thermal stability is found to increase with progressive addition of SrO into glass matrix by the increase in T_g as revealed by DTA analysis. The increase in T_g represents network polymerization. Thus, the addition of SrO improves the stability and hence the rigidity giving rise to more compact structure of the glass network.

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