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FTIR and DTA Investigations on B_2O_3-CaO-MnO_2 Glasses

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Abstract: ***Di erent glass samples were prepared in the system $60B_2O_3$-(40-x) CaO-xMnO_2 (where x=0, 5, 10, 15 and 20 mol %) employing a rapid melt-quenching technique. The effect of MnO_2 content on structure of the glasses are systematically investigated by X-ray diffraction, FTIR and DTA techniques. The amorphous nature of the samples was checked by X-Ray diffractometry. IR measurements revealed an existence of trigonal BO_3 and tetrahedral BO_4 structural units. The glass transition temperature (T_g) of the samples was found to decrease with increase MnO_2 content, The results of above studies show that the manganese ions distrubed the bonds connecting in the binary glass and hence, some of the BO_4 units converted into BO_3 units, which means that MnO_2 plays the role of network modifier in the structural network.***
Keywords: XRD, FTIR, DTA.

I. INTRODUCTION

Glass materials are one of the possible alternatives to concrete because they can be transparent to visible light and their properties can be changed by composition of modifier oxides and preparation techniques. The structure of borate glasses was studied by many researchers [1] and reported that B_2O_3composed of BO_3 units forming three-member (boroxol) rings. 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 the primary building blocks in all borate glasses. The physical properties of borate glasses can often be altered by the addition of a network modifier to the basic constituents [2] - [4].

CaO containing glass possesses higher refractive index, and exhibits high optical basicity, large polarizability and large nonlinear optical susceptibility [5]. CaO 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. Calcium borate glasses are great in potential for their industrial and technological applications, infrared transmitting materials or as active medium of Raman fibre optical amplifiers and oscillators [7].

Transition Metal Ions (TMIs) containing glasses have attracted great attention because of their numerous applications in memory switching, electrical threshold, optical switching devices etc., [8]. Among TMIs, a manganese ion has strong bearing on optical, electrical and magnetic properties [9]. It is used to probe glass structure and exhibits different valance states in different glass matrices depending on quantitative properties of glass formers and modifiers, ion size in glass matrices, field strength and mobility of the cations Mn^{3+} and Mn^{2+} are well known paramagnetic ions while Mn^{2+} and Mn^{4+} are luminescent activators. Trivalent manganese ions in glasses exhibit octahedral coordination having large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbit, whereas divalent manganese ion with tetrahedral and octahedral coordination possesses small magnetic anisotropy due to zero angular momentum [9] – [11].

Present paper reports the experimental results of spectroscopic and thermal analyses of ternary B_2O_3-CaO-MnO_2 glass system. The X-ray diffraction is used to study the glassy nature of the samples. Infrared (IR) transmission spectra have been studied for obtaining the structural information of these glasses. The thermal behaviour of the prepared glasses was studied by differential thermal analysis (DTA) and correlated with their structure.

II. EXPERIMENTAL METHOD

A. Glass Preparation

A series of glass samples of formula $60B_2O_3$-(40-x) CaO-xMnO_2 (where x=0, 5, 10, 15 and 20 mol %) were prepared using rapid melt-quenching technique. The analytical reagent grade powders of boron trioxide (B_2O_3), calcium oxide (CaO) and manganese dioxide (MnO_2) were mixed in the appropriate composition (The nomenclature and composition of glasses are given in Table 1).

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The powders were mixed thoroughly and then melted in a silica crucible for 3 hours in muffle furnace at 900°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 obtained samples are ready for characterization. The amorphous nature of the samples is confirmed by X-ray diffraction technique using Philips (Philips PW 1050/51) X-ray powder diffractometer with CuKα radiation. The infrared transmission spectra of the glasses are measured by KBr pellet technique at room temperature in the wave number range 400-4000 cm^{-1} by a Fourier Transform computerised infra-red spectrometer type (Perkin Elmer FTIR spectrometer model RX-1). Differential thermal analysis (DTA) has been carried out using SDT-Q600 version 8.0 instruments at a heating rate of 20°c/min in nitrogen gas atmosphere.

Table.1: Nomenclature and composition of glasses

Sample No	Nomenclature	Composition in mol%			Remarks
		B_2O_3	CaO	MnO_2	
1	BC	60	0	40	
2	BCM05	60	5	35	
3	BCM10	60	10	30	Mol% of B_2O_3 is constant
4	BCM15	60	15	25	
5	BCM 20	60	20	20	

III. RESULTS AND DISCUSSION

A. XRD analysis

The XRD patterns of BCM05 and BCM20are shown in fig 1. The absence of Bragg's peak in the XRD patterns confirmed that the prepared samples are amorphous and homogeneous in nature [12], [13].

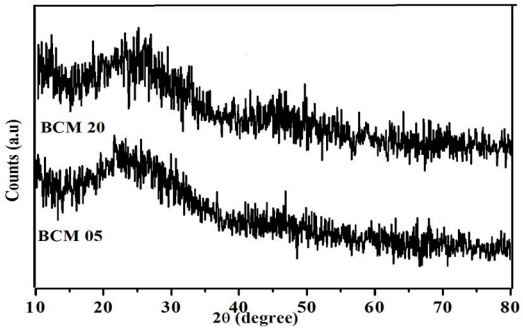


Fig.1. XRD pattern of BCM05 and BCM20 glasses

B. FTIR Studies

The infrared spectra of the glasses are measured at room temperature in the wavenumber range 400-4000 cm^{-1} as shown in the Fig.2. The vibrational modes of the borate glass network show the presence of three infrared spectral regions. It consists of two conventional bands and one additional band observed due to the presence of borate groups. The first group of band in the region 1200-1500 cm^{-1} is due to the asymmetric stretching vibration of the B-O bond of trigonal BO_3 units containing non-bridging oxygenion. Second group lies between 800 and 1200 cm^{-1} is due to the B-O bond stretching of the tetrahedral BO_4 units. The third group is observed around 700 cm^{-1} and is due to bending of B-O-B linkages in the borate network [14]. The peak at 806 cm^{-1} is found missing in the FTIR spectra of BCM 05 glass, which indicates the absence of boroxol rings in the network. This is due to the addition of CaO to B_2O_3 breaks these rings and hence consists of only BO_3 and BO_4 groups [15].

In the present glasses, the bands in the region 1299cm^{-1}-1374cm^{-1} are assigned to symmetric stretching vibration of B-O bonds in BO_3 structural units and the bands between 924cm^{-1} and 1044 cm^{-1} are due to the stretching vibration of BO_4 units. The intensity of the first group of bands increases and the second group of bands is decreases with the increase in the content of MnO_2 at the expense of CaO, which is due to the conversion of tetrahedral BO_4 units to trigonal and also formation of weak B-O-M linkages. This means that MnO_2 enter the network as glass modifier. The weak band around ~650cm^{-1} is assigned to the B-O-B bending vibrations of BO_3 groups. An addition bands in the region extend from 400 to 500cm^{-1} is assigned to the vibration of metal cation in bivalent state.

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Table2: Band positions and their corresponding assignments of prepared glasses

Wavenumber (cm^{-1})	Assignment
~1299-1374	B–O stretching vibration of B-O bond of BO_4 units from boroxol rings
~924 -1044	B–O stretching vibration of BO_4 units in tri-, tetra- and pentaborate groups
~650	B-O-B bending vibrations
~400-500	Vibration of metal cation

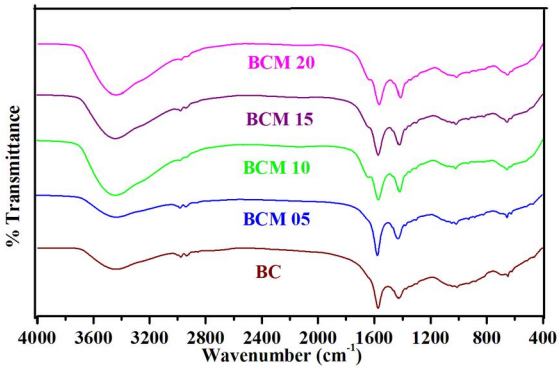


Fig.2. FTIR spectra for prepared glasses with different concentrations of MnO_2

C. Thermal Analysis

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 exhibits a small endothermic hump at lower temperature in this glass samples, which are characteristic of glass transition temperature (T_g) region followed by a single exothermic peak at high temperature and is characteristic of crystallization temperature (T_c). The exothermic peak is followed by endothermic peak, which is characteristic of the melting temperature(T_m). Glass transition temperature is one of the fundamental properties related to the viscosity of the glass and considerably dependent on the composition of the glass. From the table 3, the values of T_g, T_c and T_m decrease from 274°C to 220°C, 543°C to 351°C and 904°C to 749°C with the substitutions of MnO_2 into BCM glass matrix respectively. Values T_g, T_c and T_m decrease with increasing manganese ions in place of calcium ions weakness the borate network and hence the glass structure. The stability factor and Hruby's parameter of the studied glasses are shown in Table3. Hruby's parameter gives the information on the stability of the glass against devitrification. The values of S and K_{gl}, decrease with increasing MnO_2. This indicates the formation of BO_3 units, which decreases the network dimensionality and connectivity of the glass network.

Table 3: Values of T_g, T_c, T_m, S and K_{gl} of BCM glasses

Name of the sample	Glass transition temperature' (T_g°/C)	Crystallization temperature (T_c°/C)	Melting temperature (T_m°/C)	Thermal stability (S)	Hruby's parameter (K_{gl})
BC40	274	543	904	269	0.7451
BCM05	264	495	836	231	0.6774
BCM10	254	422	805	168	0.4386
BCM15	238	380	798	142	0.3397
BCM20	220	351	749	131	0.3291

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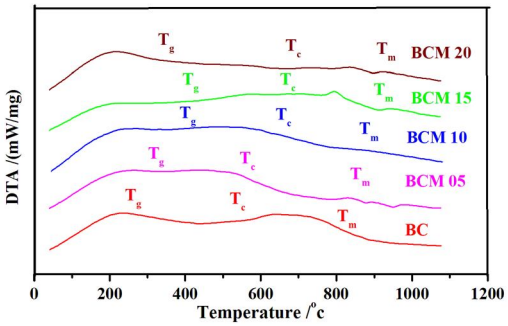


Fig.3. DTA curves of BCM glasses

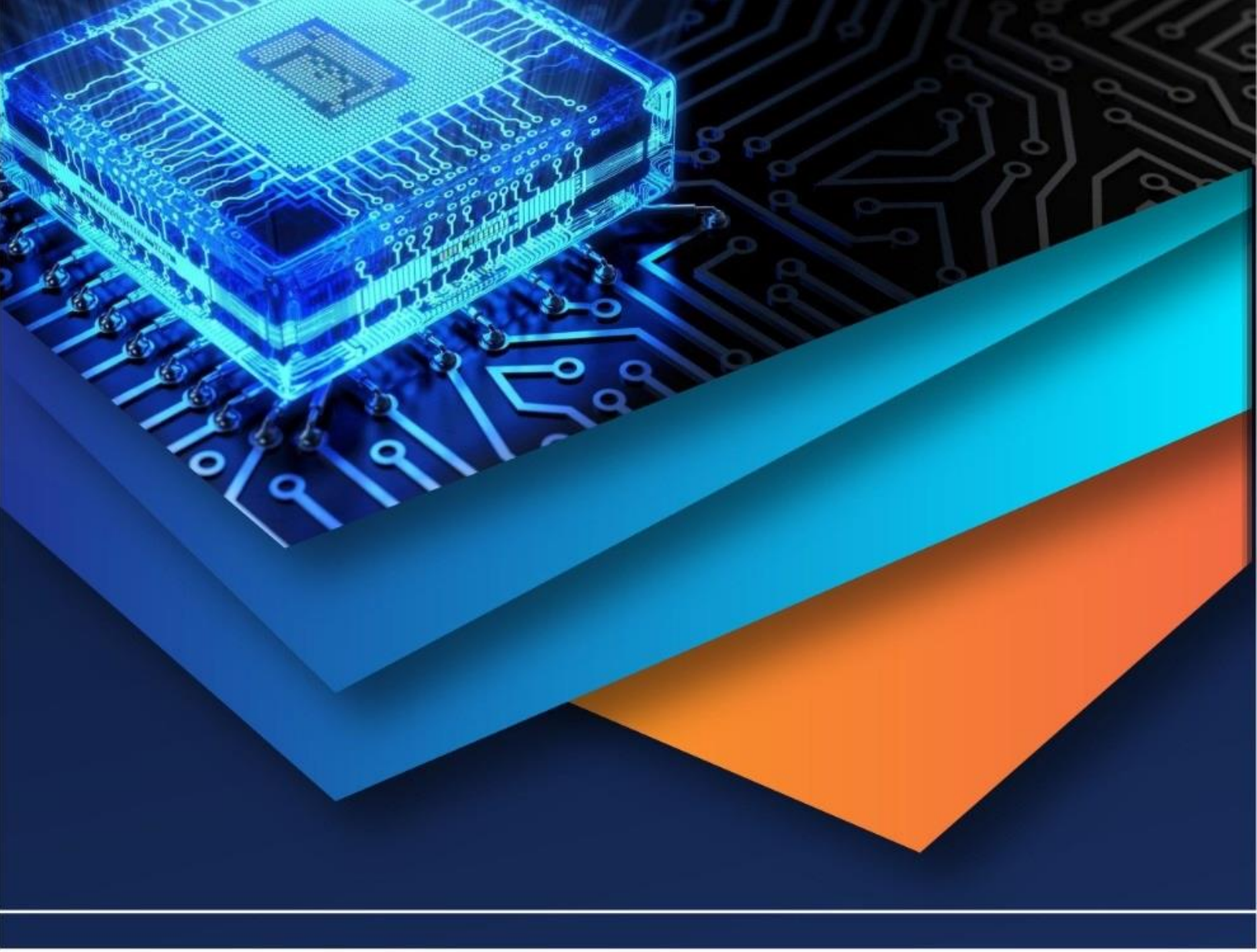
IV. CONCLUSION

The glass samples of composition B_2O_3-CaO-MnO_2 have been successfully developed which is transparent and moisture resistant. From the XRD profiles, the amorphous nature of the glass sample is confirmed. The presence of BO_3 and BO_4 structural units are observed from the traces of IR spectra. Differential thermal analysis depicted a decrease in T_g, T_c, T_m stability and Hruby's parameter with the successive replacement of CaO by MnO_2 and account for an increase in three-dimensional linkage and degree of disorder in the glass network.

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