

Synthesis and Characterization of $\text{CuO-MnO}_2\text{-B}_2\text{O}_3$ Glasses

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Abstract

A Series of $\text{CuO-MnO}_2\text{-B}_2\text{O}_3$ glasses containing 5-30 mol% of CuO were synthesized by sudden quenching method. The glass samples prepared were characterized by X-ray diffraction (X-RD), Infrared spectra (IR) and Differential thermal analysis (DTA) techniques. From X-RD, all the samples were found to be completely amorphous in nature. The infrared spectra of the glasses were studied in the wave number range 400 to 4000 cm^{-1} in an attempt to study their structure systematically. No compositional dependence was observed in the structure. The small shift in the peak frequencies was observed. No boroxol ring formation was observed in the structure of these glasses. The formation of B-O bond (stretching) was indicated. It was concluded that the structure of borate glasses consists of randomly connected BO_3 triangles but absence of BO_4 (tetraborate) groups. From DTA study the glass transition temperature (T_g) and glass melting temperature (T_m) were determined. T_g and T_m for all the glasses were found to be composition dependent.

Keywords : $\text{CuO-MnO}_2\text{-B}_2\text{O}_3$ glasses, X-RD, IR, DTA.

1. Introduction

The glasses have a prominent role in the field of electronics and have wide applications in industry, space research, computer memories etc. when the electronically conducting oxide glasses were discovered, glass formation and properties in transition metal oxide systems have been extensively studied due to their important semiconducting behaviour [1-4] Chaudhury et al [5] have discussed in brief the general procedure for making glass ceramic superconductors and some of their physical properties. Ghosh et al[6] discussed the results of dc-conductivity of semiconducting vanadium bismuth oxide glasses on the basis of polaronic hopping models. Dc-conductivity density and infrared investigation have been carried out on $\text{ZnO-PbO-B}_2\text{O}_3$ glasses by Dowelder et al [7]. Infrared spectra of zinc doped lead borate glasses have been studied by Motke et al [8] Structural and physical properties of $\text{Fe}_2\text{O}_3\text{-B}_2\text{O}_3\text{-V}_2\text{O}_5$ glasses were studied by Kundu et al [9] ESR, IR and optical absorption studies on $\text{X Na}_2\text{O-(50 - X) ZnO-50B}_2\text{O}_3$ ternary glasses have been carried out by Chinnababu et al[10]. Infrared, ESR and optical absorption studies of $\text{TeO}_2\text{-ZnO-NaF}$ glass system have been reported Kamalakar et al[11]. Structural investigation of $\text{CuO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses by FTIR, Raman and UV-VIS spectroscopes were studied by Ardelean et al[12] . Thermal and optical properties $\text{CuO-BaO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses were studied by Takebe et al [13]. Structural characterization of Borate glasses containing zinc and manganese oxides were carried out by Pal et al [14]. The effect of copper ions addition on structural and optical properties of zinc borate glasses was studied by Stefan et al [15].

Soppe et al[16] suggested that, the structure of borate glasses heavily depends upon the cooling rate of the melt through the range of glass transition temperature. DTA study of barium borovanadate glasses has been done by Bansal et al[17] to determine structure of the glass. DTA was used to determine the crystallization temperature of $\text{BaO-TiO}_2\text{-B}_2\text{O}_3$ glass system by Bhargawa et al[18].

In the present paper the structure of $\text{CuO-MnO}_2\text{-B}_2\text{O}_3$ glasses is discussed with the help of infrared spectra and differential thermal analysis. Since infrared spectroscopy is the most advantageous tool for the study of amorphous materials, we have used it to determine the structure of borate glasses containing varying amounts of CuO.

2. Experimental

2.1 Sample preparation

The glass samples under investigation were prepared in a fireclay crucible. The muffle furnace used was of Heatreat Co. Ltd. (India) operating on 230 volts A.C. reaching upto a maximum temperature of $1500 + 10^{\circ}\text{C}$. Glasses were prepared from A R grade chemicals. Homogenous mixture of an appropriate amounts of CuO , MnO_2 and B_2O_3 (mole%) in powder form was prepared. Then, it was transferred to fire-clay crucible which was subjected to melting temperature (1300°C). The duration of melting was generally two hours. The homogenized molten glass was cast in steel disc of diameter 2 cm and thickness 0.7 cm. Samples were quenched at 200°C and obtained in glass state by sudden quenching method. All the samples were annealed at 350°C for two hours.

More details regarding the preparation of glass samples has been reported elsewhere.[19,20,21,22]. The general formula was $\text{XCuO}-20\text{MnO}_2-(80-\text{X})\text{B}_2\text{O}_3$, where $x = 5, 10, 15, 25, 30$ mol%. From X-RD it was found that the nature of samples was amorphous.

X-ray diffraction (X-RD)

The X-ray diffractograms of all glasses were obtained from R.S.I.C., Nagpur University, Nagpur. The large angle X-RD curves were recorded using Phillips X-ray powder diffractometer PW1730 and target $\text{Cu K}\alpha$ radiation. The results were recorded using a PM 8208A chart recorder and an A 100 (Digital) printer with VT125 terminal simultaneously. The details of the operating conditions were as follows :

KV and mA ---- 35 KV and 20 mA, Scanning speed ---- $0.04^{\circ} 2\theta/\text{sec}$, Scanning angle ---- 10° to 95° , Range (RFS) ---- 2000 cps, Recorder speed ---- 5 mm/deg 2θ

X-ray diffraction technique was used to check the possible crystallinity of the samples after quenching and annealing. All the glass samples were found to be completely amorphous in nature.

Infrared spectra (IR)

The infrared spectra of all the glasses are studied in the wave number range 400 to 4000 cm^{-1} on Perkin Elemer IR spectrometer 467 at Dept of chemistry, Institute of Science, Mumbai. The KBr pellet technique was used. The resolution was 1 cm^{-1} . From the IR spectra, different group positions are determined.

Differential Thermal Analysis (DTA)

DTA study of all the samples is done on DTA unit at R.S.I.C., Nagpur University, Nagpur. The experimental conditions for DTA of the glasses are given below :

No. of glasses scanned –one, Quantity of the sample-32 to 80 mg, Rate of scanning - $10^{\circ}\text{C}/\text{min}$, temperature range- room temperature to 600°C , Atmosphere- air, Reference sample taken $\alpha\text{Al}_2\text{O}_3$ (Alumina) powder. From DTA study, the glass transition temperature (T_g) and glass melting temperature (T_m) are determined.

3. Results and Discussion

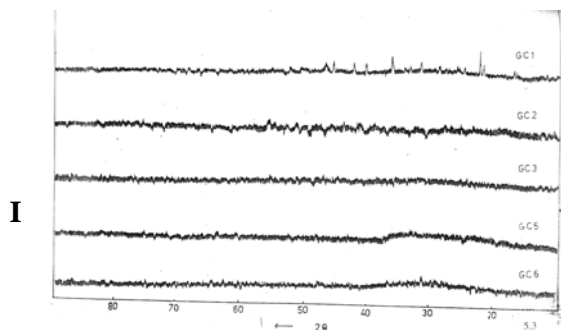


Figure 1 – X-RD curves of the glass samples.

The X-RD patterns of the glasses studied are given in Fig. 1. In the present work X-RD technique has been used only to check the amorphous nature of the samples. It is well known that

Table 1 : Experimental data obtained from X-RD patterns

Glass No.	Percent Crystallinity	Remark
GC1	1.3	All Samples are amorphous in nature
GC2	Nil	
GC3	Nil	
GC5	Nil	
GC6	Nil	

the absence of sharp peak in intensity versus 2θ curves indicates amorphous nature of glass sample. Indication of sharp peaks in the curve suggests the formation of phases in the glass during annealing time or slow cooling. In X-ray diffraction spectra no peaks have been observed so all the glass samples studied are perfectly amorphous in nature except glass GC1 is 1.3% crystalline, which is negligibly small and hence it can also be regarded as mostly amorphous in nature (Table 1)

The infrared spectra of the glass samples are shown in Fig. 2. The frequency corresponding to peak positions for all the glasses are given in Table 2. It is observed that the basic structure of the glass remains same throughout the series i.e. no compositional dependence is observed in the structure. The small shift in the peak frequencies is observed.

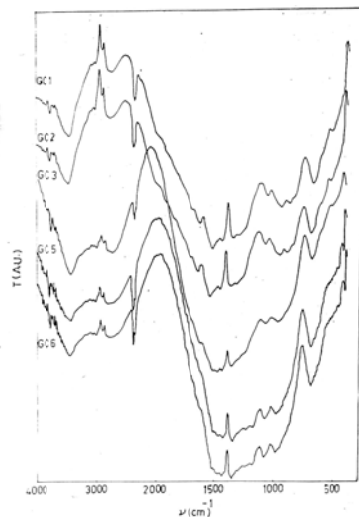


Figure 2 – IR- absorption spectra of the glass samples.

Table 2 : Experimental data obtained from IR-absorption spectra

Glass No.	Peak Positions (cm) ⁻¹											
	1	2	3	4	5	6	7	8	9	10	11	12
GC1	426 ^w	553 ^w	666 ^w	866 ^w	966 ^w	1066 ^w	1213 ^w	1326 ^w	1453 ^m	1513 ^w	1626 ^w	2326 ^m
GC2	423 ^w	500 ^w	675 ^s	890 ^w	941 ^m	1055 ^w	1220 ^w	1340 ^w	1434 ^m	1515 ^w	1622 ^m	2358 ^m
GC3	426 ^w	526 ^w	666 ^w	866 ^w	966 ^w	1039 ^m	1226 ^w	1326 ^w	1453 ^m	1513 ^w	1626 ^w	2313 ^m
GC5	466 ^w	522 ^m	680 ^m	853 ^w	978 ^w	1068 ^m	1220 ^w	1348 ^m	1423 ^w	1471 ^m	1610 ^m	2366 ^s
GC6	445 ^w	566 ^w	679 ^m	890 ^w	979 ^m	1074 ^w	1220 ^w	1342 ^w	1424 ^w	1526 ^w	1610 ^w	2363 ^s

It is known that B₂O₃ is a basic glass former, trivalent, has higher bond strength lower action size (0.23A⁰). The main structural units of borate glasses are BO₃ groups and they form a planer triangular structure[23]. Soppe et al[16] have suggested that, the structure of borate glasses heavily depends upon rate of cooling of the melt through the range of the glass transition temperature. The oxygen boron ratio changes due to the addition of other oxides in the form of impurity in B₂O₃ glass. The increase in the oxygen-boron ratio changes the BO₃ triangles to BO₄[16]. According to Krogh-Moe model (1969) the structure of boron oxide glass consists of a random network of planer BO₃ triangles, with a certain fration of six membered (boroxol) rings[24, 25]. X ray and neutron diffraction data suggest that, glass structure consists of random network of BO₃ triangles without boroxol rings. Similar findings have also been reported from the molecular dynamics studies by Soules[26] and Amini et al[27].

In all the glass samples studied, five to nine absorption peaks are observed. The shape of the peaks are strong, medium and weak.

In the glasses studied, the absence of boroxol rings have been confirmed on the basis of absence of peak frequency at 806 cm⁻¹ in the IR spectra. This is attributed to the progressive

substitution of boroxol rings (boron only in III coordination) by triborate and tetraborate groups (boron simultaneously in III and IV co-ordination) [28]. On passing from boron trioxide to borate glasses, a change in the coordination number of the boron takes place. In the glasses, the boron is tetrahedrally surrounded by four oxygen atoms[29]. The structure of $\text{CuO-B}_2\text{O}_3$ glass changes by the addition of MnO_2 . In all the glasses, absorption peaks in the range $1300 - 1356 \text{ cm}^{-1}$ indicate the formation of B-O bond (stretching) which has the bond length 1.38 \AA [16]. The series of glass samples show bands around 960 cm^{-1} suggesting fundamental frequency of $(\text{BO}_3)^{3-}$ group. The absorption peaks in the range $600-900 \text{ cm}^{-1}$ are due to bending of O-B-O. This possibility is more in borate glasses where there are no boroxol rings and increases when the structure is built up with randomly connected BO_3 triangles[16]. The absorption peak at 670 cm^{-1} in the glass series indicates plane bending of BO_3 . the absence of absorption peak at 378 cm^{-1} suggests the absence of BO_4 (tetraborate) group. The absorption peak at 1066 cm^{-1} is attributed to the fundamental frequency ν_3 of BO_4 stretching and ν_2 of B-O bond. The new modes appear around 950 cm^{-1} which is related to borate groups containing BO_4 (tetrahedra) [30]. The absence of absorption band at 772 cm^{-1} indicates the absence of the formation of six membered borate rings containing one tetrahedral boron[31]. Raman bands in the region $900-1100 \text{ cm}^{-1}$ appear in borate glasses containing tetrahedral borons[32]. So the weak and broad band around 940 cm^{-1} can be attributed to the boron-oxygen stretching of tetrahedrally co-ordinated boron. Bhargava et al[33] observed a weak band around 662 cm^{-1} and assigned it as arising due to the metaborate group.

In IR absorption of B_2O_3 glass this band near 656 cm^{-1} is attributed to the bond bending vibration of the B-O-B linkage[34] Similar band is observed in all the glass samples studied here. In the series the addition of MnO_2 contents affect the structure of glasses. This is observed to be due to the presence of absorption peak at $1220, 1226$ and 1526 cm^{-1} . The formation of CuO bond is observed, which is confirmed from absorption band in the range $460-485 \text{ cm}^{-1}$ [35]. It is concluded that the structure of borate glasses consists of randomly connected BO_3 triangles. The formation of randomly connected boroxol rings do not appear in our investigation, these finding are in agreement with those of Mozi et al[25].

In the present work, DTA technique has been employed to determine glass transition temperature (T_g), glass melting temperature (T_m) and to test the possibility of formation of crystallization and phase separation in borate glasses. The DTA curves of the glass samples are given in Fig. 3. Thermal data obtained from DTA curves is given in Table 3.

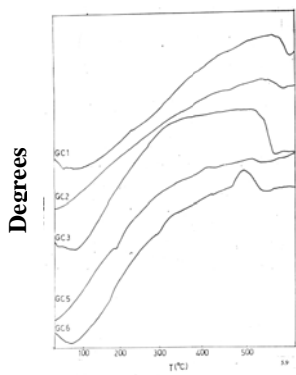


Figure 3 – DTA- curves of glass samples.

Table 3 : Thermal data obtained from DTA curves

Glass No.	Glass transition temperature T_g ($^{\circ}\text{C}$)	Glass melting temperature $T_m = 1.5 T_g$ ($^{\circ}\text{C}$)
GC1	538	807
GC2	530	795
GC3	498	747
GC5	472	708
GC6	498	747

The first endotherm (step) obtained at a lower temperature corresponds to the glass transition, the onset, of the former representing, the thermal glass transition temperature [36]. The glass transition temperatures of different glasses lie in the range of $472-538^{\circ}\text{C}$. The value of T_g decreases with increasing CuO content. Using the relation $T_m = 1.5 T_g$ [37] the melting temperatures (T_m) of different glasses are calculated and reported in table 3. the absence of the first exotherm after first small step in all the curves suggests that there occurs no crystallization during thermal cycling at the time of DTA[38]. If the maximum crystallization occurs during the annealing of glasses it can be detected from this peak.

The third endothermic peak after second, corresponds to melting of small crystallites in the sample[39]. The absence of the peaks in DTA curves of all the glass samples indicates that the samples were perfectly amorphous in nature during thermal cycling at the time of DTA.

The glass transition temperature depends on the strength and connectivity of the network[40,41]. The values of T_g for the glasses studied here are in well agreement with the values reported by many workers for borate and other glasses[16, 40, 42, 43, 44]. It is concluded that the values of T_g and T_m for all the glasses studied are composition dependent. No crystallization occurs during thermal cycling at the time of DTA. All the glass samples are perfectly amorphous in nature.

4. Conclusions

It is concluded that the $\text{CuO-MnO}_2\text{-B}_2\text{O}_3$ glasses studied are perfectly amorphous in nature. The structure of borate glasses consists of randomly connected BO_3 triangles. The structure of present glass system is independent of composition. Very small change in the absorption bands may occur that do not account for major structural changes. No boroxol ring formation is observed. The values of glass transition temperature (T_g) and glass melting temperature (T_m) for the glasses are found to be composition dependent.

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