Structural and Dielectric Properties of Cuo-Mno2-B2o3 Glasses

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ABSTRACT:

Series of CuO-MnO2-B2O3 glasses containing 5-30 mol% of CuO were synthesized by sudden quenching method. The glass samples ready were characterized by diffraction (X-RD), Infrared spectra (IR) and Differential thermal analysis (DTA) techniques. From X-RD, all the samples were found to be utterly amorphous in nature. The infrared spectra of the glasses were studied within the frequency vary four hundred to 4000 cm-1 in a trial to The small shift within the peak frequencies was discovered. Review their structure consistently. No compositional dependence was observed in the structure. The small shift within the peak frequencies was discovered. No boroxol ring formation was discovered within the structure of those glasses. The formation of B-O bond (stretching) was indicated. It was concluded that the structure of borate glasses consists of randomly connected BO3 triangles but absence of BO4 (tetra borate) groups. From DTA study the glass transition temperature (Tg) and glass melting temperature (Tm) were determined. Tg and thulium for all the glasses were found to be composition dependent. . The values of nonconductor constant are totally different temperature (313-573K) at a relentless frequency of one kHz area unit according. It is observed that the dielectric constant is independent of temperature up to certain temperature range, but after that the dielectric constant increases with temperature rapidly. The dielectric constant of all the samples studies found to be composition dependent. In the glasses studied dipole relaxation development is discovered

Keywords : CuO-MnO_2-B_2O_3glasses, X-RD, IR, DTA, Dielectric constant

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 chemical compound glasses were discovered, glass formation and properties in transition metal chemical compound systems are extensively

studied because of their necessary semi conductive behavior [1-4] Chaudhury et al [5] have mentioned in short the final procedure for creating glass ceramic superconductors and a few of their physical properties. Ghosh et al[6] mentioned the results of dc-conductivity of semi conductive atomic number 23 atomic number 83 chemical compound glasses on the idea of polaronic hopping models. Dc-conductivity density and infrared investigation are administered on ZnO-PbO-B2O3 glasses by Dowelder et al [7]. Infrared spectra of metal doped lead salt glasses are studied by Motke et al [8] Stuctural and physical properties of Fe2O3-B2O3-V2O5 glasses were studied by Kundu et al [9] ESR, IR and optical absorption studieds on X Na2O-(50 â€“ X) ZnO-50B2O3 ternary glasses have been carried out by Chinnababu et al[10]. Infrared, ESR and optical absorption studies of TeO2-ZnO-NaF glass system are according Kamalakar et al[11]. Structural investigation of CuO-Bi2O3-B2O3 glasses by FTIR, Raman and UV-VIS spectroscopes were studied by Ardelean et al[12] . Thermal and optical properties CuO-BaO-B2O3 â€“P2O5 glasses were studied by Takebe et al [13]. Stuctural characterization of salt glasses containing metal and atomic number 25 oxides were administered by Pal et al [14]. The impact of copper ions addition on structural and optical properties of metal salt 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 soften through the vary of glass transition temperature. DTA study of atomic number 56 borovanadate glasses has been done by Bansal et al[17] to work out structure of the glass. DTA was wont to confirm the crystallization temperature of BaO-TiO2-B2O3 glass system by Bhargawa et al[18]. In the gift paper the structure of CuO-MnO2-B2O3 glasses is mentioned with the assistance of infrared spectra and differential thermal analysis. Since infrared spectrographic analysis is that 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. Mandaletal [45] have according the nonconductor behavior of glass system BaO-PbO-TiO2-B2O3-SiO2. The electric relaxation study of V2O5-B2O3 glasses has been done by singh et al [46].

2.EXPERIMENTAL:

2.1 Sample preparation:

The glass samples under investigation were prepared in a fireclay crucible. The muffle chamber used was of Heatreat Co. Ltd. (India) operating on 230 volts A.C. reaching upto a most temperature of 1500 + 10oC. Glasses were prepared from A R grade chemicals. Homogenous mixture of associate acceptable amounts of CuO, MnO2 and B2O3 (mole%) in powder form was prepared. Then, it had been transferred to fire-clay vessel that was subjected to melting temperature (1300OC). The duration of melting was generally two hours. The homogenized melted glass was solid in steel disc of diameter two cm and thickness zero.7 cm. Samples were quenched at 200OC and obtained in glass state by fast extinction methodology. All the samples were tempered at 350O C for 2 hours. More details concerning the preparation of glass samples has been according elsewhere.[19,20,21,22]. The general formula was

XCuO-20MnO2-(80-X) B2O3, where x = 5, 10, 15, 25, 30 mol%. From X-RD it had been found that the character of samples was amorphous.

2.2 X-ray diffraction (X-RD):

The X-ray diffract grams 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 diffract meter PW1730 and target Cu K 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 ---- 0.04O 2 /sec , Scanning angle ---- 10O to 95O, Range (RFS) ---- 2000 cps, Recorder speed ---- 5 mm/deg 2/sec. X-ray diffraction technique was wont to check the attainable crystalline of the samples when extinction and hardening. All the glass samples were found to be utterly amorphous in nature.

2.3 Infrared spectra (IR):

The infrared spectra of all the glasses are studied in the wave number range 400 to 4000 cm-1 on Perkin ElemerTheKBr pellet technique was used. The resolution was 1 cm-1. From the IR spectra, totally different cluster positions area unit determined.

2.4 Differential Thermal Analysis (DTA):

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

No. of glasses scanned –one, Quantity of the sample-32 to 80 mg, Rate of scanning - 10Oc/min, temperature range- room temperature to 600O C, Atmosphere- air, Reference sample taken Al2O3 (Alumina) powder. From DTA study, the glass transition temperature (Tg) and glass melting temperature (Tm) ar determined.

2.5 Dielectric Constant :

The nonconductor constant of the glass was measured by measurement the capacitance of the samples at constant frequency one kHz within the temperature vary 313 to 573K. Digital LCR meter 925, systronics created (India), was used for the measure of capacitance. The accuracy within the capacitance measure was ±0.1 pF.

Table 1 : Experimental data obtained from X-RD patterns

S.NO	Glass No	Percent Crystallinity	Remark
1	GC1	1.3	All Samples are amorphous in nature
2	GC2	Nil	
3	GC3	Nil	
4	GC5	Nil	
5	GC6	Nil	

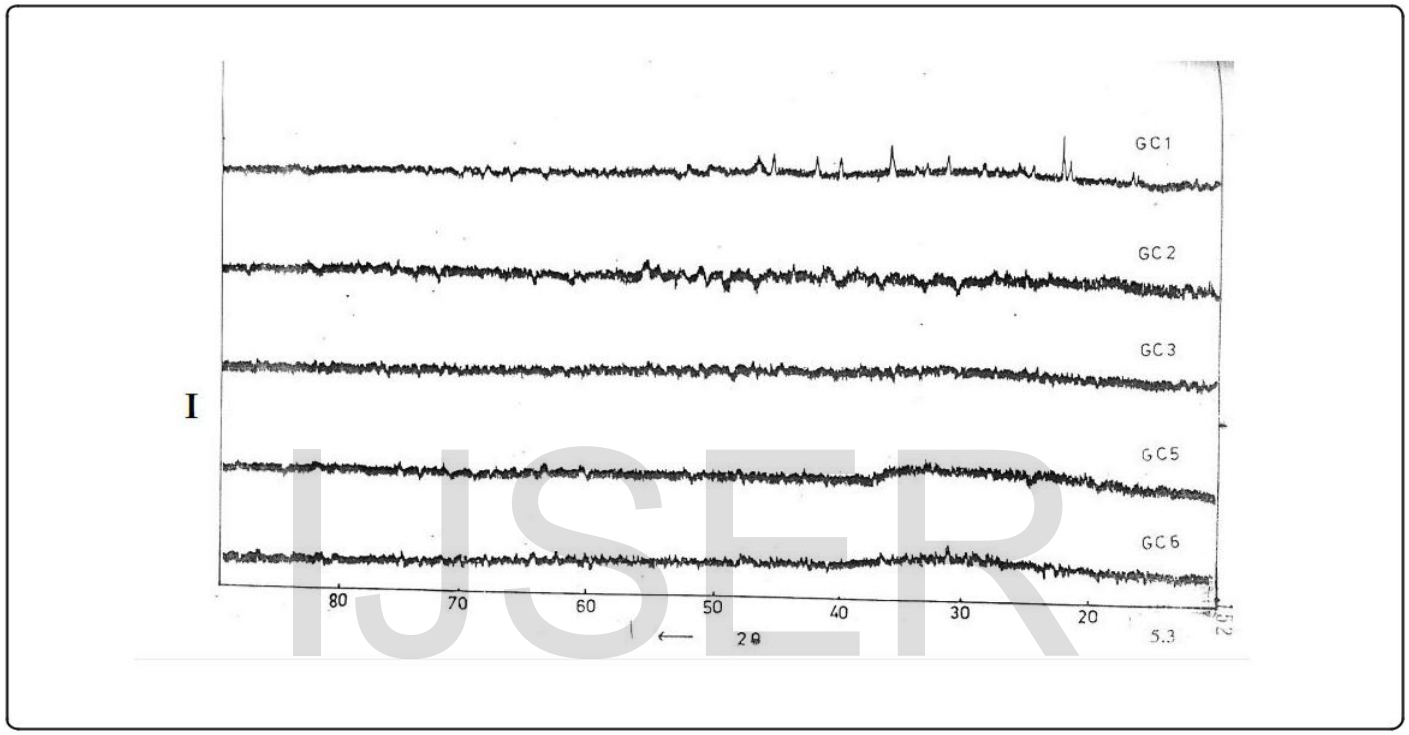

Figure 1 :X-RD curves of the glass samples.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction (X-RD):

The X-RD patterns of the glasses studied ar given in Fig. 1. In the gift work X-RD technique has been used solely to envision the amorphous nature of the samples. It is well known that the absence of sharp peak in intensity versus 2 curves indicates amorphous nature of glass sample. Indication of sharp peaks within the curve suggests the formation of phases within the glass throughout hardening time or slow cooling. In X-ray diffraction spectra no peaks are ascertained thus all the glass samples studied ar dead amorphous in nature except glass GC1 is one.3% crystalline, which is negligibly small and therefore it may also be considered principally amorphous in nature (Table 1).

3.2 Infrared spectra (IR):

The infrared spectra of the glass samples ar shown in Fig. 2.The frequency such as peak positions for all the glasses ar given in Table two. It is ascertained that the essential structure of the glass remains same throughout the series i.e. no compositional dependence is observed in the structure. The small shift within the peak frequencies is ascertained. It is renowned that B2O3 could be a basic glass former, trivalent, has higher bond strength lower action size (0.23AO). The main structural units of salt glasses ar BO3 teams and that they type a planing machine triangular structure[23]. Soppe et al[16] have steered that, the structure of borate glasses heavily depends upon rate of cooling of the melt through the range of the glass transition temperature. The element element quantitative relation changes because of the addition of alternative oxides within the variety of impurity in B2O3 glass. The increase within the oxygen-boron quantitative relation changes the BO3 triangles to BO4[16]. According to Krogh-Moe model (1969) the structure of element chemical compound glass consists of a random network of planing machine BO3 triangles, with a precise fration of six five-membered (boroxol) rings[24, 25]. X ray and nucleon optical phenomenon knowledge counsel that, glass structure consists of random network of BO3 triangles while not boroxol rings. Simi lar 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 ar sturdy, 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 solely in III coordination) by triborate and tetraborate teams (boron at the same time in III and IV co-ordination) [28]. On passing from element oxide to salt glasses, a amendment within the coordination variety of the element takes place. In the glasses, the boron is tetrahedrally surrounded by four oxygen atoms[29]. The structure of CuO-B2O3 glass changes by the addition of MnO2. In all the glasses, absorption peaks in the range 1300 – 1356 cm-1 indicate the formation of B-O bond (stretching) which has the bond length 1.38 AO [16]. The series of glass samples show bands around 960 cm-1 suggesting fundamental frequency of (BO3)3- group. The absorption peaks within the vary 600-900 cm-1 ar because of bending of O-B-O. This chance is a lot of in salt glasses wherever there aren't any boroxol rings and will increase once the structure is made up with every which way connected BO3 triangles[16]. The absorption peak at 670 cm-1 within the glass series indicates plane bending of BO3. the absence of absorption peak at 378 cm-1 suggests the absence of BO4 (tetraborate) cluster. The absorption peak at 1066 cm-1 is attributed to the fundamental frequency 3 of BO4 stretching and 2 of B-O bond.

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Figure 2 : IR- Obsorption spectra of the glass samples

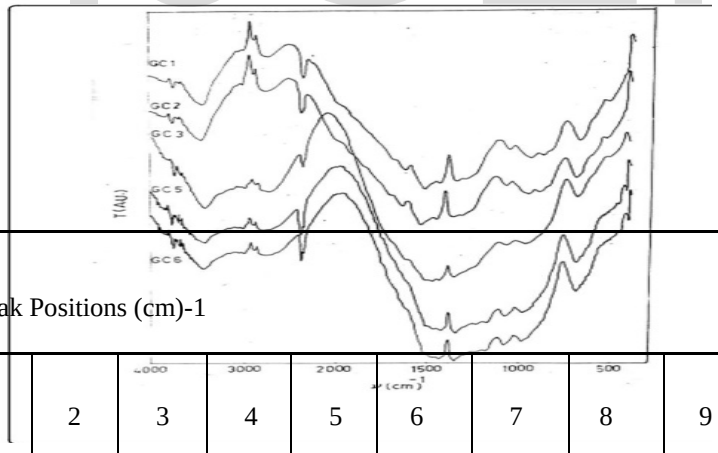

Table 2 : Experimental data obtained from IR-absorption spectra

GlassNo.	Peak Positions (cm)-1											
	1	2	3	4	5	6	7	8	9	10	11	12
GC1	426w	553w	666w	866w	966w	1066w	1213w	1326w	1453m	1513w	1626w	2326m
GC2	423w	500w	675s	890w	941m	1055w	1220w	1340w	1434m	1515w	1622m	2358m
GC3	426w	526w	666w	866w	966w	1039m	1226w	1326w	1453m	1513w	1626w	2313m

GC5	466w	522m	680m	853w	978w	1068m	1220w	1348m	1423w	1471m	1610m	2366s
GC6	445w	566w	679m	890w	979m	1074w	1220w	1342w	1424w	1526w	1610w	2363s

The new modes seem around 950cm-1 that is expounded to salt teams containing BO4 (tetrahedra) [30]. The absence of optical phenomenon at 772 cm-1 indicates the absence of the formation of six five-membered salt rings containing one tetrahydralboron[31]. Raman bands within the region 900-1100 cm-1 seem in salt glasses containing tetrahedral borons [32]. So the weak and broad band around 940 cm-1 are often attributed to the element-oxygen stretching of tetrahedrally co-ordinated boron. Bhargava et al[33] ascertained a weak band around 662 cm-1 and assigned it as arising because of the metaborate cluster. In IR absorption of B2O3 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 MnO2 contents have an effect on the structure of glasses. This is discovered to ensue to the presence of absorption peak at 1220, 1226 and 1526 cm-1. The formation of CuO bond is discovered, which is confirmed from absorption band in the range 460-485 cm-1 [35]. It is all over that the structure of salt glasses consists of arbitrarily connected BO3 triangles. The formation of arbitrarily connected boroxol rings don't seem in our investigation, these finding are in agreement with those of Mozi et al[25].

3.3 Differential Thermal Analysis (DTA):

In the gift work, DTA technique has been employed to determine glass transition temperature (Tg), glass melting temperature (Tm) and to test the possibility of formation of crystallization and phase separation in borate glasses. The DTA curves of the glass samples area unit given in Fig. 3. Thermal knowledge obtained from DTA curves is given in Table3

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 transitiontemperatures of various glasses dwell the vary of 472-538OC. The value of Tg decreases with increasing CuO content. Using the relation Tm = one.5 Tg [37] the melting temperatures (Tm) of different glasses are calculated and reported in table 3. the absence of initial|the primary} exotherm once first tiny step altogether the curves suggests that there happens no crystallization throughout thermal sport at the time of DTA[38]. If the most crystallization happens throughout the tempering of glasses it will be detected from this peak.

The third endothermal peak once 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.

Table 3 : Thermal data obtained from DTA curves

Glass No.	Glass transition temperature Tg (0C)	Glass melting temperature Tm = 1.5 Tg (^{0}C)
GC1	538	807
GC2	530	795
GC3	498	747
GC5	472	708
GC6	498	747

Figure 3 – DTA- curves of glass samples.

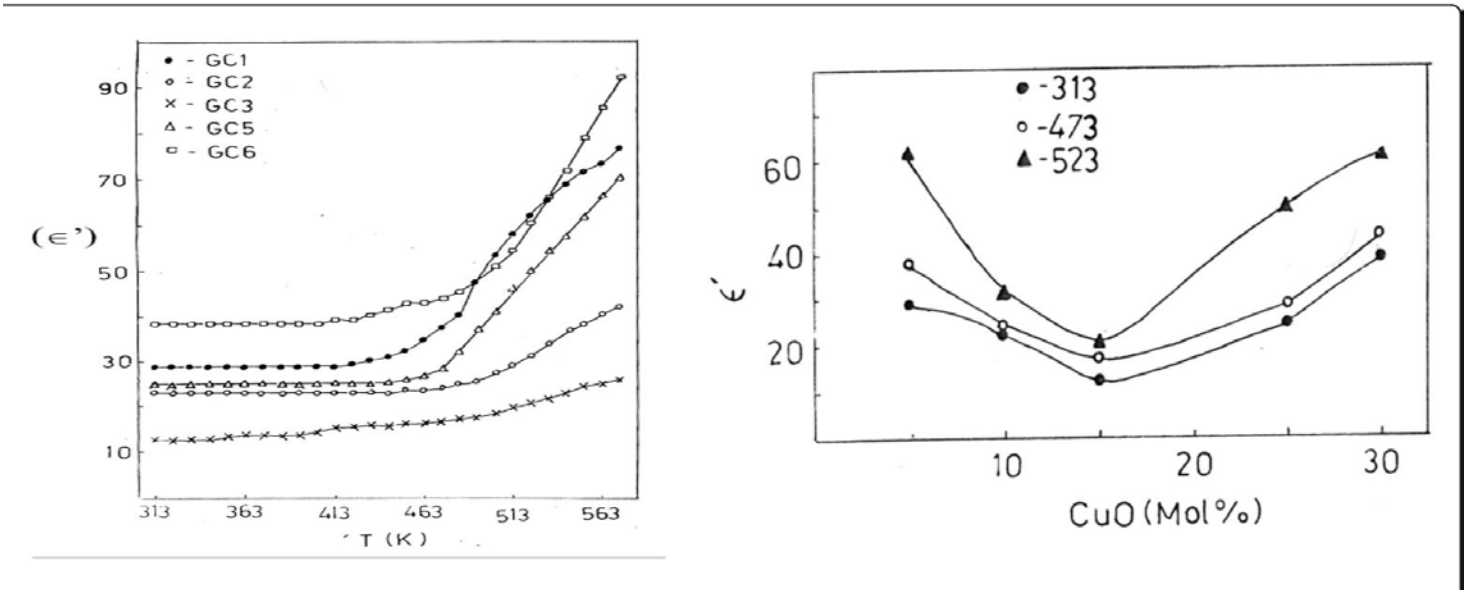

Fig. 4 **Fig. 5**

Fig 4 : Variation of dielectric constant with temperature at constant frequency of 1KHz for the glass samples
Fig 5 : Variation of dielectric constant with composition at a constant temperature for the glass samples

The glass transition temperature depends on the strength and property of the network[40,41]. The values of Tg for the glasses studied here area unit in well agreement with the values reportable by several staff for salt and different glasses[16, 40, 42, 43, 44]. It is all over that the values of Tg and Tm for all the glasses studied area unit composition dependent. No crystallization happens throughout thermal sport at the time of DTA. All the glass samples area unit utterly amorphous in nature.

3.4 Dielectric Constant:

The variation of dielectric constant (') atdifferent temperature (313-573K) at a constant frequency of 1 KHz for the glass samples is shown in Fig. 4. It is observed that the dielectric contant(') is independent of temperature upto certain temperature range, but after that the dielectric constant increases with temperature rapidly. A similar trend has been reportable for various transition metal compound glasses by Sayer et al [4], Mansingh et al [47]. This increase in stuff constant is partially thanks to a amendment in electronic structure and partially thanks to thermal enlargement. In glasses rise of temperature could increase the free carrier density to introduce physical phenomenon losses. The change in the dielectric constant in the view of independent composition, very cash within the absorption bands could occur that don't account for major structural changes. No boroxol ring formation is observed. The values of glass transition temperature (Tg) and glass melting temperature (Tm) for the glasses area unit found to be composition dependent. The stuff constant of the glass samples is found to be temperature and composition dependent. In the glasses dipole relaxation phenomenon is observed. high temperature could be a characteristics of Debye sort relaxation method wherever symmetrical distribution of time constant takes place. The speedy rise is probably going to arise from the opposite sources of polarization probably from increased conductor polarization as temperature rises. More sharp rise of (') at high temperature was also observed in other oxide glasses by Sunder et al [48] and Singh et al [46]. The stuff constant of the entire sample studied is found to be composition dependent. Variation of stuff constant with composition at a relentless temperature is shown in figure five. A dip is discovered at fifteen mildew of CuO. In these glasses dipole relaxation phenomenon is observed.

CONCLUSION

It is all over that the CuO-MnO2-B2O3 glasses studied area unit utterly amorophous in nature. The structure of salt glasses consists of arbitrarily connected BO3 triangles. The structure of gift glass system is freelance of composition. Very small change in theabsorption bands may occur that do not account for major structural changes. No boroxol ring formation is observed. The values of glass transition temperature (Tg) and glass melting temperature (Tm) for the glasses are found to be composition dependent. The dielectric constant of the glass samples is found to be temperature and composition dependent. In the glasses dipole relaxation phenomenon is observed

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