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STRUCTURAL AND THERMAL PROPERTIES OF CALCIUM DOPED BORATE GLASSES

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Abstract: A Series of B_2O_3-CaO-CuO glasses containing 5-20 mol% of CuO were prepared by sudden quenching method and characterized by X-Ray Diffraction (XRD), Infrared spectroscopy (IR) and Differential Thermal Analysis (DTA) techniques. From XRD studies, the samples were found to be completely amorphous in nature. The infrared spectra of the glasses were recorded in the wave number range 400 to 4000cm^{-1} as an attempt to study their structure systematically. The IR measurements revealed an existences of trigonal BO_3 Pyramid, tetrahedral BO_4 and Cu^{2+} ions. Thermal properties of the glasses were studied using differential thermal analysis. Composition dependence of the DTA data are disussed in the light of rigidity of the glasses.

Keywords: Borate glasses, CuO ,XRD, IR, DTA

I. INTRODUCTION

Glasses containing B_2O_3 are of great interest because of their wide applications [1]. Borate glasses are considered to be structurally more encouraging and found them as good candidates in doping them with varied amounts of alkali, alkaline and transition materials for various applications. The structure of borate glasses consists of a random network of boroxol rings and BO_3 triangles connected by B-O-B linkages. When suitable modifiers of alkali, alkaline and transition metal oxides are doped, the boroxol rings broken and borate structural units(BO_3 and BO_4) are formed [2]. Transition metal oxides exhibits interesting properties and are used in a wide variety of applications. Transition metals such as cadmium, copper etc., doped glasses show semiconducting properties [3-6].These glasses are potential candidates for electrical memory and optical switching devices [7,8], cathode materials for making solid state devices and optical fibers [9,10].In different glasses, copper can exist as a monovalent (Cu^+) ion or as a divalent (Cu^{2+}) ion or containing both states and even metallic copper as in copper ruby glass. The stability of both frequent Cu^+ and Cu^{2+} ions are found to be sensitive to the glass type, composition and environment or condition of melting [11]. Although most glasses melt under ordinary atmospheric condition, they are usually assumed not to contain metallic copper. Many investigators have reported that copper may exist in glass network both as a network former and also as a network modifier[12]. Drzewiecki, A., Padlyak[13] have reported that the valance state of copper modifies not only chemical and physical properties, but also the glass forming ability and the glasses containing copper ions in different oxidation states are highly useful in electrical memory switching devices. Recently, Cu^{2+} ions doped glasses have drawn a great attention because of their optical stability and electrical applications[14]. In light of aforementioned one, the aim of the present work is to understand the effect of copper oxide on the structural bahaviour of Calcium borate glasses. The structural studies have been done with the help of XRD, FTIR and DTA analyses.

II. EXPERIMENTAL

Sample preparation

Batches of copper doped calcium borate glasses were prepared using conventional melt quenching technique. The required quantities of AR grade B_2O_3, CaO and CuO were wieghed by using electronic balance. The weighed amounts of all the chemicals were mixed by using an agate mortar and transferred into silica crucible in an electrically heated furnace at 900°C. The obtained glass samples were annealed at 350°C for 2 hours to remove any external stresses. Then the oven was switched off and glass was allowed to cool gradually to room temperature. The obtained samples were ready for characterization. The nomenclature and composition of the glasses is given in Table 1.

Table 1 : Nomenclature and composition of glasses

Sample No.	Nomenclature	Composition in mol%			Remarks
		B_2O_3	CaO	CuO	
1	BCCu05	60	35	5	Mol% of B_2O_3 is constant
2	BCCu10	60	30	10	
3	BCCu15	60	25	15	
4	BCCu20	60	20	20	

III. RESULTS AND DISCUSSION

III.1. X-Ray Diffraction Analysis

X-ray diffraction technique was used to check the possible crystallinity of the samples after quenching and annealing. It is well known that the absence of sharp peak in intensity versus 2θ curves indicates amorphous nature of glass samples. In the recorded spectra, no peaks have been observed so the glass samples studied are perfectly amorphous in nature .

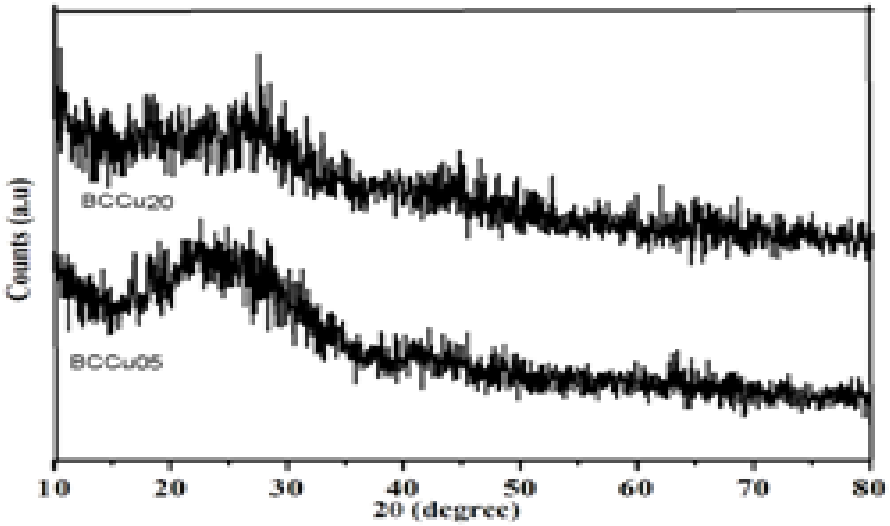


Fig 1. XRD pattern of BCCu05 and BCCu20 glasses

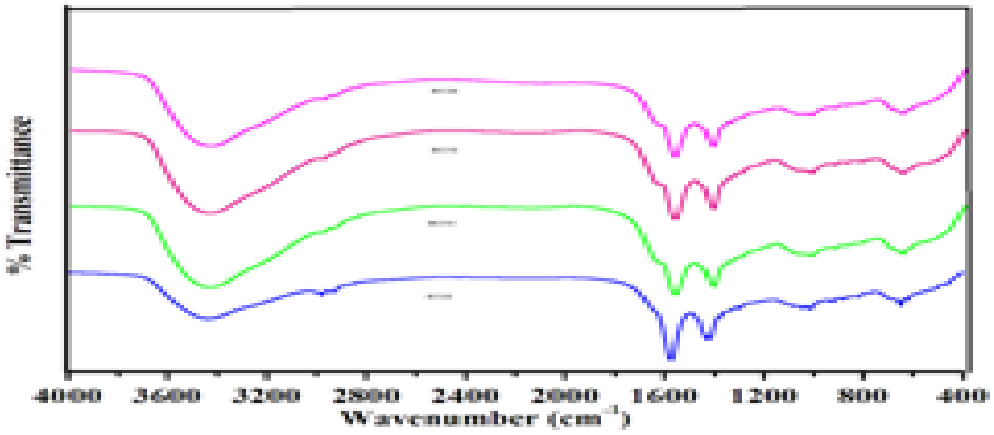
III.2.FTIR Spectroscopy

Fourier Transform-Infrared Spectroscopy (FTIR) is an analytical technique used to identify the functional groups present in the glass. The infrared spectra of the glass samples are shown in Fig. 2. The band positions and their corresponding assignments are given in Table 2. .

In the present glasses different peaks are observed. The shape of the peaks are strong, medium and weak. The band at 1347cm^{-1} is attributed to the B-O bonds due to stretching vibrations of trigonal BO_3 units[15,16] in the borate network, whereas the observed band around 1077cm^{-1} is due to stretching vibrations of the B-O bonds in BO_4 units. The another band around 720cm^{-1} is due to the bending vibration of B-O-B linkages. The addition of CuO at the expense of CaO, a new band is formed at 470cm^{-1} . This band is attributed to vibrations of Cu^{+}-O and Cu^{2+}-O for samples containing CuO. The gradual substitution of copper oxide makes an increase in the intensity of vibrational band due to BO_4 group at the expense of BO_3, indicating increase in the compactness of the glass network.

Table2: Band positions and their corresponding assignments of prepared glasses.

Wavenumber (cm^{-1})	Assignment
~1347	B-O stretching vibrations of the trigonal BO_3 units
~1077	B–O stretching vibration of B-O bond of BO_4 units from boroxol rings
~720	B-O-B bending vibrations of B-O-B linkages
~470	Specific vibration of Cu^{+}-O and Cu^{2+}-O



III.3. Differential Thermal Analysis (DTA)

DTA technique has been employed to determine glass transition temperature, glass melting temperature 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.

The DTA exhibits a small endotherimic hump at lower temperature in the glass sample, which is characteristic of glass transition temperature(T_g) region followed by a exotherimic peak and is characteristic of crystallization temperature(T_c). The exothermic followed by a endothermic peak which characteristic of a melting temperature (T_m). The value of T_g, T_c and T_m increase from 364°C to 468°C , 635°C to 792°C and 866°C to 986°C with an increase CuO at the expense of CaO, implies that the number of bridging oxygen group increases and makes the glasses more compact.

Table 3: Values of glass transition temperature, crystallization temperature, melting temperature, thermal stability and Hruby's parameter of various glass samples

Name of the sample	Glass transition temperature'(℃)	Crystallization temperature(℃)	Melting temperature(℃)	Thermal stability (S)	Hruby's parameter(K_{gl})
BCCu05	364	635	866	271	1.1731
BCCu10	371	665	889	294	1.3125
BCCu15	404	717	914	313	1.5888
BCCu20	468	792	986	324	1.6701

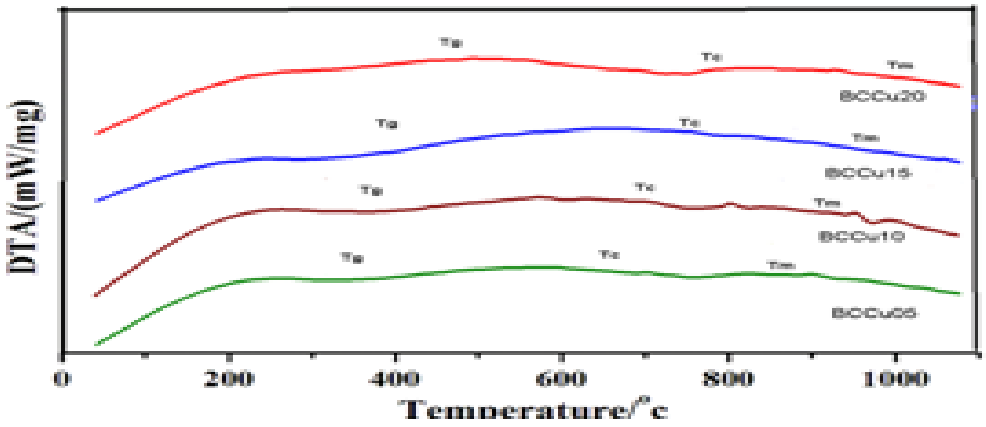


Fig.3. DTA curves for BCCu Glasses

IV. CONCLUSION

The following conclusions are drawn from the present study. XRD confirms the amorphous nature of the glass samples. IR spectra indicate that the structural role played by the boron and copper ions. A Progressive conversion of BO_3 to BO_4 structural units are also observed from the traces of IR spectra. Differential thermal analysis depicted an increase in T_g,T_c,T_m stability and Hruby's parameter with an increse in BO_4 structural unite and rigidity of the glass network.

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