

Effect of Na₂O on Structural and Thermal Properties of Cadmium Borate Glasses

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Abstract: Na₂O doped cadmium borate glasses were prepared by standard melt quench method with the composition 70B₂O₃-(30-x)CdO-xNa₂O (where x=0, 5,10,15 and 20 mol %).The prepared glass samples are subjected to characterization such as XRD, SEM, FTIR and DTA techniques. XRD and SEM reveal the amorphous nature of the glass samples. Various band positions are confirmed by FTIR and the fraction of BO₄ units increases at the expense of BO₃ structural units with the increasing concentration of Na₂O. The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature(T_m) are determined using DTA analysis. Thermal stability factor against devitrification is calculated using T_g, T_c and T_m values.

Keywords: XRD, SEM, FTIR, DTA

I. Introduction

Borate based glasses has been widely explored in recent decades owing due its proved efficiency in terms of ease of preparation, high transparency, high ionic conduction, inexpensive and relative stability[1]. Moreover, borate glass is a good host for different metals via. alkali, alkaline, transition and rare earth. Numerous efforts have been done to enhance the efficiency of the borate glass. These efforts were focused on adding modifiers and/or activators. The addition of small amount of transition metals in the glass network influenced its properties to substantial extent. This enhancement is attributed to the unfilled outer d-electron that has broad radial distributions. These transition metals exist in more than one valence states and further enhance the response to the surrounding stimuli. In view of these fact, the utilization of transition metals as activators have undergone extensive investigation in advanced technologies such as phosphors, lasers, solar energy converters and in a number of electronic devices [2, 3]. Among various transition metals, cadmium oxide is divalent in nature and acts both as the network former and modifier depending upon the composition and the host material. They stabilize the glass structure and improve its properties [4, 5]. Cd-ions are typically present in the Cd²⁺ state; however Cd⁰ and Cd⁺ may be formed under reduced conditions [6]. Glasses based on cadmium have interesting electronic transport and optical properties [7,8]. Binary cadmium borate and phosphate glasses [8,9] as well as ternary cadmium zinc-phosphate glasses are reported to be amorphous semiconductors, whereas cadmium borogermanate and borosilicate glasses are known to exhibit ohmic photoconductivity [10-12]. The addition of alkali ions as modifiers in borate glasses, break up the continuous amorphous glass-forming network and causes a gradual change in the co-ordination number of boron from three to four and further addition of alkali oxide causes the production of NBOs and increases the expansion coefficient and decrease in viscosity [13].The created cations will not be tightly bound to the network as like multivalent network -forming cations rather primarily fills the 'holes' created by the random orientation of oxygen polyhedral. Since these cations occupy the intrinsic positions they form a closely packed network structure. The structure of alkali borate strongly depends upon the species of alkali ion [14]. Alkali borate glasses are highly useful materials for vacuum ultraviolet optics and semiconductor lithography owing to the presence of stable glass forming range and transparency from the near UV to the middle infrared region [15]. The authors are interested to study the influence of Na₂O on cadmium borate glass system by various characterization technique such as XRD, SEM, FTIR and DTA.

II. Experimental

2.1 Preparation of glasses

The glass composition 70B₂O₃-(30-x) CdO-xNa₂O with different Na₂O contents (where x =5, 10, 15, 20 and 25 mol %) have been prepared by melt quenching technique. Required quantities of Analar grade B₂O₃, CdO and Na₂O were ground repeatedly using an agate mortar to achieve good homogeneity. The mixture was melted in a porcelain crucible in an electrically heated furnace under ordinary atmospheric conditions at 900° C. The obtained glass samples were annealed at 350 °C for 2 hours to remove any internal stresses. The bubble free liquid was casted into prewarmed copper mould to obtain the glass samples of dimension 6mm thickness and 10mm diameter and subjected to smooth polish. The polished samples were ready for characterization. The nomenclature and composition of the prepared glasses are given in Table 1.

2.2 Characterization techniques

The amorphous nature of the samples is confirmed by X-ray diffraction technique using diffractometers de rayons X- Inel- Equinox 1000 at a range of $2\theta=(10-100)$ degrees utilizing copper radiation with operating voltage of 40 Kv 30 mA anode current. The morphology of the samples was examined using Scanning Electron Microscope (SEM) with an acceleration voltage of 20 kv and working distance of 20-26 mm at high vacuum (HV) mode. The materials for investigation is hot air oven dried for about 1 hour at 110 °C, then coated with the help of gold coater using JEOL auto fine coater model JES-1600, coating time is 120 seconds, 10 mA and deposited with a thin layer of gold on the sample and later taken for examination. The infrared spectra of the powdered glasses were recorded at room temperature (303K) in the wavenumber range 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹ by RX1 Perkin Elemer FTIR spectrometer using KBr pellet technique. The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of these glasses were determined by differential thermal analyser NETZSCH-STA449FS JUPITER instrument at a heating rate of 20 °C/min in nitrogen gas atmosphere.

Table 1. Nomenclature and composition of glass samples

S. No.	Nomenclature	Composition in mol%	Remarks
1	BCd	70 -30	
2	BCdN05	70 - 25 - 05	Mol% of B ₂ O ₃ is constant
3	BCdN10	70 - 20 - 10	
4	BCdN15	70 - 15 - 15	
5	BCdN20	70 - 10 - 20	

III. Results And Discussion

3.1 XRD analysis

The XRD patterns of BCd, BCd05 and BCd20 glasses are 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. Moreover, the broad humps indicate that there is an existence of short range order in the glass [16].

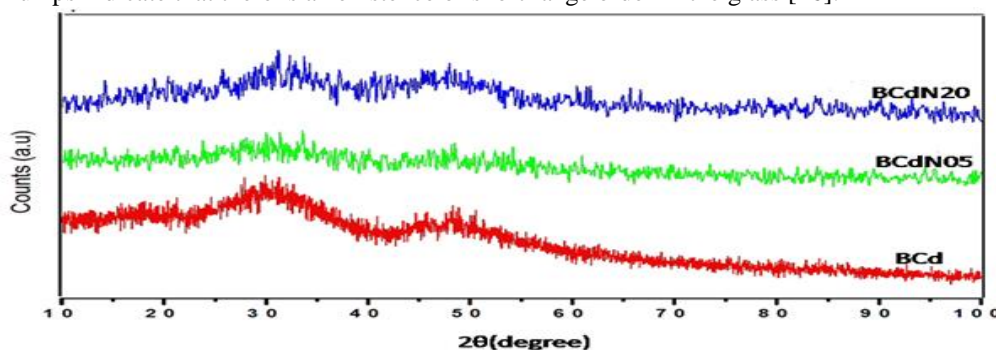


Fig. 1 X-Ray diffractogram for BCd, BCdN05 and BCdN20 glasses

3.2 SEM analysis

The morphological investigation of the prepared glass samples, are taken using SEM as shown in Fig 2. From the pictures, it is observed that different sized grain particles are distributed and the size of the particles varies in each micrograph. The particles are extremely angular and spherical in nature. Some sphere like agglomerates were found spreading in the glass surface, due to the deposition of amorphous apatite. These results are in agreement with the information provided by the XRD patterns.

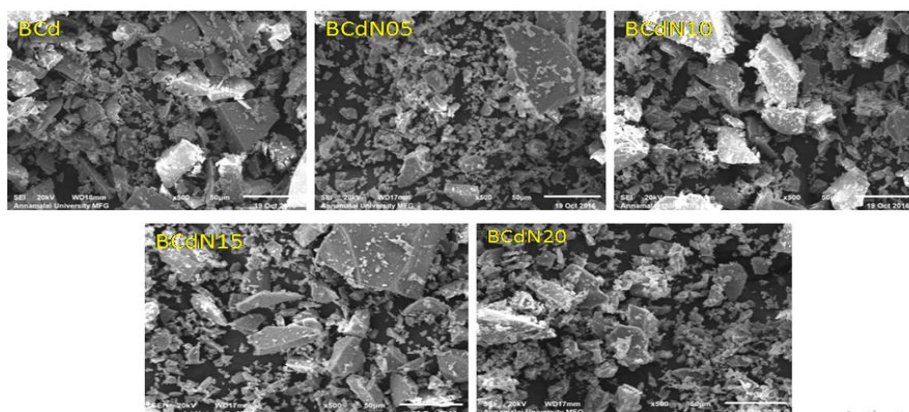


Fig.2. SEM photograph of the prepared glasses

3.3 FTIR analysis

FTIR spectra of BCd and BCdN glasses are shown in the Fig.3. The broadening of the IR-spectra indicates that there is no detectable variation in peak position to crystallization. The bands observed around 1348 cm⁻¹ corresponds to B-O bond stretching vibrations of trigonal units [17] whereas the band around 1003 cm⁻¹ [18] is assigned as B-O bond stretching vibrations of BO₄ units and the band around 710 cm⁻¹ is assigned to the bending vibrations of B-O-B linkages [19].

The intensity of the band due to BO₄ structural units has been observed to increase at the expense of the band due to BO₃ units. This observation suggests with the gradual increase in the concentration of sodium oxide, as a modifier in the glass network enhances the tetrahedral sites in the glass matrix. A new band around 450 cm⁻¹ is observed which corresponds to the tetrahedral vibrations of CdO [20]. The characteristic band at 806 cm⁻¹ of vitreous B₂O₃ of asymmetric stretching vibration of boroxol ring is found missing in the spectra which indicate the absence of boroxol ring. The band around 2700-3600 cm⁻¹ is attributed to the molecular water or BOH vibrations. The above results indicate that Na₂O though act as modifier, occupy the interstitial position and account for closed network as reported by Kamitani [21] through his IR studies on alkali oxide borate (Li₂O, Na₂O, K₂O). Since the concentration of Na₂O is restricted upto 20 mol% only tetrahedral coordination is more pronounced.

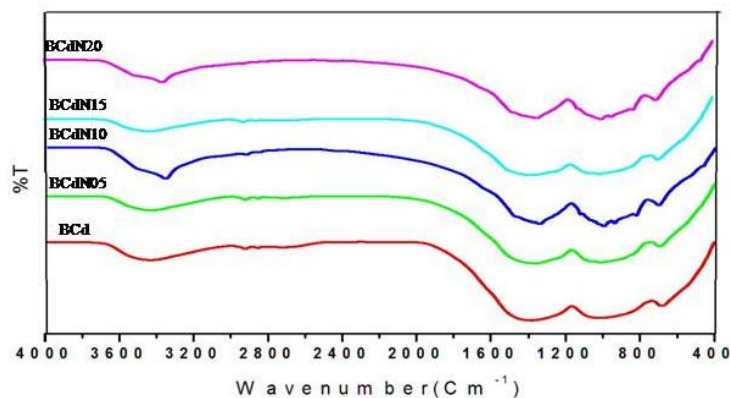


Fig.3 FTIR spectra for 70B₂O₃ - (30-x) CdO-xNa₂O glass samples

3.4 Thermal studies

Fig 4. show the DTA curves of the studied glasses. The values of glass transition temperature T_g , the crystallization temperature T_c , and melting temperature T_m , from the curves are summarized in the Table 2, which in addition gives the thermal stability range ($T_c - T_g$) as an estimate of glass stability and the Hruby's parameter (ability of the glass against devitrification). The dependence of these parameters on the composition is reflected in the DTA curve and its T_g is better understood by considering the T_g of the oxide glass that depends on the bond strength, cross-link density and closeness of packing of the glass [22].

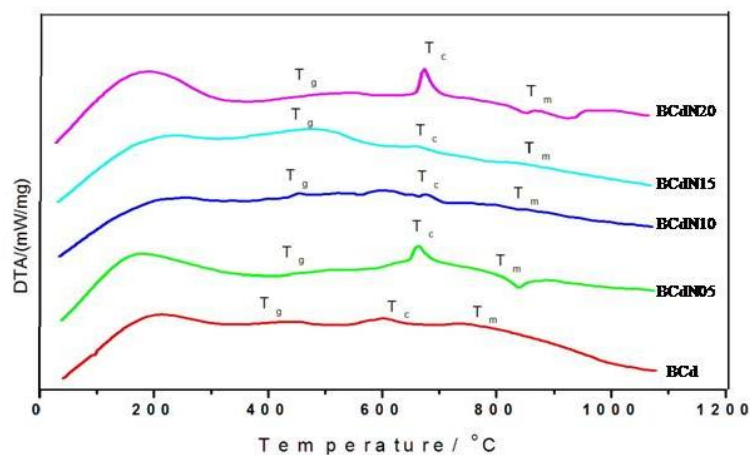


Fig.4. DTA curve for prepared glass samples

Table 2. Values of glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), thermal stability (S) and Hruby's parameter (K_{gl}) of BCdN glasses

Name of the sample	Glass transition temperature $T_g/^\circ\text{C}$	Crystallization temperature $T_c/^\circ\text{C}$	Melting temperature $T_m/^\circ\text{C}$	Thermal stability S	Hruby's parameter K_{gl}
BCd	380	632	741	252	2.3119
BCdN05	398	689	808	291	2.4454
BCdN10	409	701	812	292	2.6306
BCdN15	413	713	820	300	2.8037
BCdN20	417	722	827	305	2.9048

For the present glass system, the progressive substitution of Na₂O with higher bond strength (256.1 ± 16.7) in place of CdO with lower bond strength (235.6 ± 83.7) increases T_g . Similarly the thermal stability and the Hruby's parameter also increase.

IV. Conclusion

The following conclusions are drawn from the present study. XRD and SEM confirms the amorphous nature of the glass samples. IR spectra indicate that the structural role played by the Na₂O and CdO ions and preferentially get incorporated as modifier and former respectively. A progressive conversion of BO₃ to BO₄ 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 the successive replacement of CdO by Na₂O and account for an increase in three-dimensional linkage and rigidity of the glass network.

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