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Research Article

STRUCTURAL AND THERMAL PROPERTIES OF B_2O_3-CdO-K_2O GLASSES

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ABSTRACT

Studies based on structural and thermal properties have been carried out with wide ranging compositions in the glass system $70B_2O_3$-(30-x) CdO-xK_2O (where x=0, 5, 10, 15 and 20), in order to understand the effect of potassium ions on the structure of cadmium borate glasses. Various characterization techniques such as XRD, SEM, FTIR and DTA are used to study the modification encountered as a result of added dopant. XRD and SEM analysis confirmed the amorphous nature and homogeneity of the sample. The results of infrared spectra indicate that Cd^{2+} and K^+ ions behave as network former and modifier respectively in the present glass system. Boron exists in both trigonal and tetrahedral units in these glasses and no boroxol ring formation takes place in the glass structure. The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature(T_m) are determined from DTA analysis and the values of glass stability and Hruby's parameter are calculated to know the stability of the glasses.

INTRODUCTION

B_2O_3 is recognized as well-built glass former, with triangular borate units mostly as boroxol groups. When alkali or alkaline earth oxides and some divalent oxides like PbO, CdO are added part of the boron is changed to tetrahedral coordination to a certain limit after which non-bridging oxygens are formed. CdO when doped with B_2O_3, the formed cadmium borate glass contain Cd^{2+} ions behaving partly as modifier CdO_6 and partly as former CdO_4 units. The major stability take place for fully polymerized glass and can be relayed to the energetic of the reaction B-O-B + Cd-O-Cd = 2(B-O-Cd) which also proposed that the B-O-Cd linkage are extra stable, relatively to the mixture of B-O-B and Cd-O-Cd relations analog to B-O-Zn reported earlier (Bahammam *et al.*, 2017). Depending on the concentration of CdO, the Cd^{2+} ions are probable to occupy network modifier positions, adding together to network forming locations with CdO_4 structural units.

It is a known phenomenon that the addition of alkali metal oxide to borate based glasses changes the coordination number of some boron atoms from three to four and leads to a transformation of trigonal units into negatively charged tetrahedral units. Both BO_3 and BO_4 units are connected by bridging-oxygen atoms and represent the smallest structural units of the glass network. The formation of two boron-oxygen tetrahedra consumes the additional oxygen provided by the alkali oxide A_2O. Since each tetrahedron is charge-deficient by minus one elementary charge, two alkali ions compensate two anionic BO_4 units. An increase in A_2O concentration results in a further transformation of boron from three- to four fold coordination. Beyond a concentration of about 25-30 mol% alkali oxide content the formation of non-bridging oxygen atoms becomes a relevant process (Vershneya, 1994; Shelby,1997). It also reported in earlier studies that with the increasing radius of the ions($r_{Li}<r_{Na}<r_K<r_{Rb}$), the glass structure shows an increasing tendency for expansion with increase in non-bridging oxygens (Frank Berkemeier, 2005).

So based on the aforementioned factors authors are much interested to study the impact created by K^+ ions on cadmium borate glasses.

Experimental

Preparation of glasses

The glass composition $70B_2O_3$-(30-x) CdO-xK_2O with different K_2O contents (where x =5, 10, 15, 20 and 25 mol%) have been prepared by melt quenching technique. Required quantities of Analar grade B_2O_3, CdO and K_2O were ground repeatedly using an agate mortar to achieve good homogeneity. The mixture was melted in a porcelain crucible in an

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electrically heated furnace under ordinary atmospheric conditions at 900 ^oC. The obtained glass samples were annealed at 350 ^oC 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.

Characterization techniques

The amorphous nature of the samples is confirmed by X-ray diffraction technique using diffractometers de rayons X- Inel-Equniox 1000 at a range of 2θ=(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 vaccum (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 wave number 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 ^oC/min in nitrogen gas atmosphere.

Table 1 Nomenclature and composition of glass samples

S. No.	Nomenclature	Composition in mol%	Remarks
1	BCdK0	70 -30	
2	BCdK05	70 - 25 - 05	
3	BCdK10	70 - 20 - 10	Mol% of B_2O_3
4	BCdK15	70 - 15 - 15	is constant
5	BCdK20	70 - 10 - 20	

RESULTS AND DISCUSSION

XRD analysis

The XRD patterns of BCdK0, BCdK05 and BCdK20 glasses are shown in Fig.1.

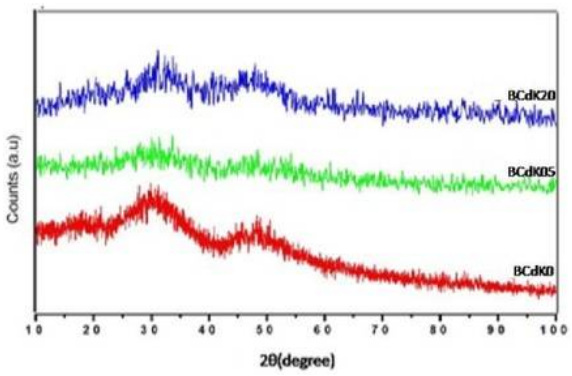

Fig. 1 X-Ray diffractogram for BCdK0, BCdK05 and BCdK20 glasses

The absence of Bragg's peak in the XRD patterns confirmed that the prepared samples are amorphous and homogeneous in nature. Moreover, the board humps indicate that there is an existence of short range order in the glass (Priyanka Goyal, 2017).

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 (Ezhil Pavai and Thirumal, 2013). These results are in agreement with the information provided by the XRD patterns.

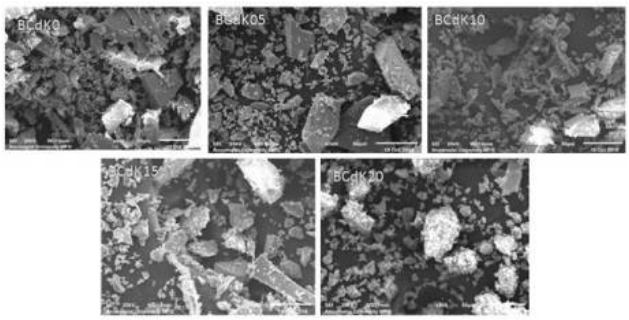

Fig.2 SEM photograph of the prepared glasses

FTIR analysis

Borate glasses generally consist of several structural groupings like [BO_3], [BO_4], boroxol rings, triborate, diborate units, etc. Thus, vibrational modes of the vitreous modified borate network are mainly active in three infrared spectral regions (Takahiro Ohkuto, *et al.*, 2016; Doweidar, *et al.*, 2013; Kamitsos, *et al.*, 1987)

- The first region in the range between1200 and 1600 cm^{-1} is due to the asymmetric stretching vibrations of B-O bond of trigonal BO_3 units containing non-bridging oxygen ions.
- The second region lies between 800 and 1200 cm^{-1} and its spectral features are due to the B-O bond stretching of the tetrahedral BO_4 units and
- The third region around 700 cm^{-1} is due to bending of B-O-B linkages in the borate network.

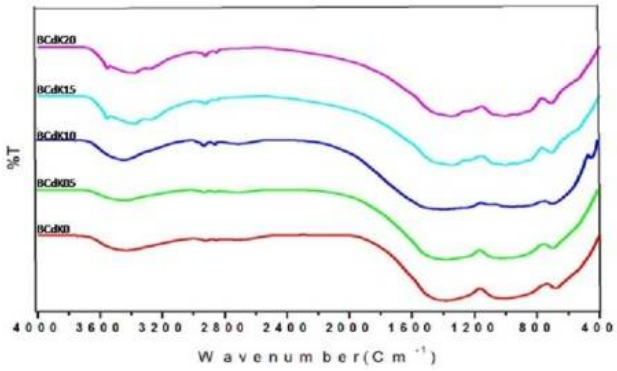

Fig 3 FTIR spectra for BCdK glass samples

Figure 3. represent the the FTIR spectra for prepared glass system. The band observed around 1375 cm^{-1} is due to the B-O stretching vibrations of trigonal BO_3 (Keerti Marita, *et al.*, 2013) units and the band around 936cm^{-1} is assigned B-O bond

stretching vibrations of BO_4 units(Samee, *et al*.,2013) and the band around 717$cm^{-1}$is due to the B-O-B linkages (Ramadevudu, *et al*., 2012). The band around 445 cm^{-1} is due the specific vibrations of K^+ ions (Edukondalu, *et al*., 2014). The absence of peak at 806 cm^{-1} indicates the absence of boroxol ring formation. The band around 2700 - 3400 cm^{-1} is attributed to the molecular water or BOH vibrations.

The introduction of alkali oxide alters the structure of the glass to a large extent by the conversion of BO_3 units present in the glass into BO_4 units and it produces a more polymerized borate network. As the concentration of alkali earth oxide increases, the intensity of the band due to [BO_3] decreases corresponding to increase in the intensity of [BO_4] units. Therefore successive replacement of CdO by K_2O modifies the B-O-B linkage to either B-O-Cd linkage or B-O-K linkage, thereby making the structure more compact.

Thermal studies

The DTA is very useful for determination of melting points of crystals and glass transformation and crystallization temperatures of glasses (Shelby, 1997). In all the glasses, the DTA curve exhibits a small endothermic hump at lower temperature in the glass samples, which is characteristic of the transition temperature (T_g). Single exothermic peak at high temperature region is characteristic of crystallization temperature (T_c) and other endothermic events corresponding to the melting temperature (T_m). Fig.4 shows the differential thermal analysis curve for BCdK glasses. From the Table 2, it is observed that the first endothermic hump appears in the region 398°C followed by exothermic peak at 650°C and another endothermic peak appears at 759°C. The values of above parameters increase with the addition of K_2O at the expense of CdO, implies that the number of bridging oxygen groups increases with more closed structures. These results suggest that K_2O acts as a network modifier and occupies the intrinsic positions.

The bond strength plays a vital role in increasing T_g congruently as the concentration of K_2O increases, thus promoting increased cross-link density between the atoms involved. The successive replacement of K_2O with higher bond strength (277.8±20.9KJ/mole) in place of CdO with lower bond strength (235.6± 83.7 KJ/mol) increases T_g. In addition thermal stability and Hruby's parameter also increases and supports the closed packed structure.

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 BCdK 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_{g1}
BCdK0	380	632	741	252	2.3119
BCdK05	398	650	759	254	2.3303
BCdK10	406	665	764	259	2.6162
BCdK15	411	677	773	266	2.7708
BCdK20	415	684	820	269	2.8021

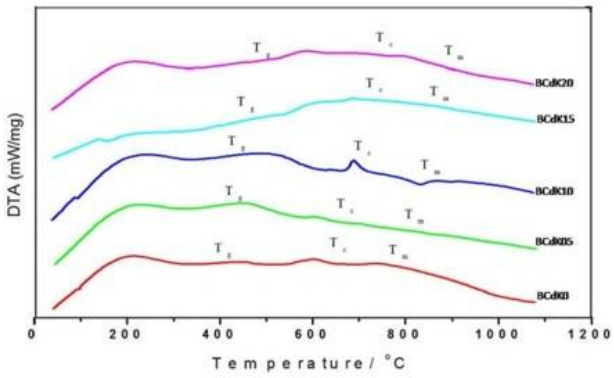

Fig.4 DTA curve for BCdK glass samples

CONCLUSION

The following conclusions are drawn from the present study. XRD and SEM confirm the amorphous nature of the glass samples. IR spectra indicate that the structural role played by the K_2O and CdO ions and preferentially get incorporated as modifier and former respectively. 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 the successive replacement of CdO by K_2O and account for an increase in three-dimensional linkage and rigidity of the glass network.

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