



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

International Journal of Recent Scientific Research
Vol. 7, Issue, 12, pp. 14502-14504, December, 2016

**International Journal of
Recent Scientific
Research**

Research Article

STRUCTURAL AND THERMAL PROPERTIES OF B_2O_3 - Na_2O - CdO TERNARY GLASSES

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ARTICLE INFO

Article History:

Received 17th September, 2016

Received in revised form 21st

October, 2016

Accepted 05th November, 2016

Published online 28th December, 2016

Key Words:

XRD, DTA, FTIR.

ABSTRACT

Sodium borate glasses of composition $70B_2O_3-(30-x)Na_2O-xCdO$ with different CdO contents (where $x = 5, 10, 15, 20$ and 25 mol%) were prepared by conventional melt quenching method. The amorphous nature of the prepared glasses was confirmed by X-ray diffraction patterns. FTIR spectra show the presence of trigonal and tetrahedral borate units and the results indicate the conversion of BO_3 to BO_4 units occurs with the increase in CdO content. Differential thermal analysis suggests that the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of the glasses increase with the increase of CdO content.

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INTRODUCTION

The boric oxide (B_2O_3) is one of the good glass formers and can form glass alone with good transparency, high chemical durability and thermal stability. The size of B^{3+} ions is very small and it can fit into the trigonal void created by three oxide ions in mutual contact, forming a BO_3 units. BO_3 units are the primary building blocks in all borate glasses. The insulating property of borate glasses turns into a semiconducting or electronic or ion conducting nature when metal oxides such as alkali oxides are added to them. Alkali borate glass systems are good candidates for ion conduction and suitable for the fabrication of solid state batteries. The role of Na_2O in the B_2O_3 network is to modify the host structure through the transformation of the structural units of the borate network. There have been several studies, which deal with the structure of sodium borate glasses [1,2].

Among various heavy metal oxides, cadmium oxide (CdO) is considered to be one of the promising candidates as a host material with a wide band gap for its development as a potential optical material [3]. CdO , a II-VI n-type semiconductor exhibits interesting properties such as large band gap, low electrical resistivity and high transmission in the visible region which makes it suitable for wide range of applications such as solar cells, photo transistors, diodes, transparent electrodes and gas sensors [4-8]. Glasses based on cadmium oxide have been studied extensively by several authors primarily because of their interesting electronic, transport and optical properties. The present work is to

investigate the role of CdO on structural and thermal properties [9] of prepared glass. The structural and thermal properties are studied using FTIR and thermal analysis.

Experimental

Preparation of glasses

The glass composition $70B_2O_3-(30-x) Na_2O-xCdO$ with different CdO 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 (99%), Na_2O (99%) and CdO (99%) 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 preheated stainless- steel 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 and the prepared glass samples are shown in Fig.1.

The amorphous nature of the samples is confirmed by X-ray diffraction technique using GE-Inspection technology 3003TT model made in Germany copper target operating voltage 40 Kv 300 mA current rate. The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of these glasses were determined by differential scanning

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calorimetric traces, recorded using thermal analyser NETZSCH-STA449FS JUPITER instrument at a heating rate of 20 °C/min in nitrogen gas atmosphere. 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 SHIMADZU 8400 FTIR spectrometer, using KBr pellet technique

Table 1 Nomenclature and composition of BNC glass samples

S. No.	Nomenclature	Composition in mol%	Remarks
1	BNC05	70-25-5	Mol% of B ₂ O ₃ is constant
2	BNC10	70-20-10	
3	BNC15	70-15-15	
4	BNC20	70-10-20	
5	BNC 25	70-05-25	



Fig. 1 Photograph of prepared glass samples

RESULTS AND DISCUSSION

XRD analysis

The XRD patterns of BNC 05 and BNC 25 glasses are shown in Fig.2. 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 [10]

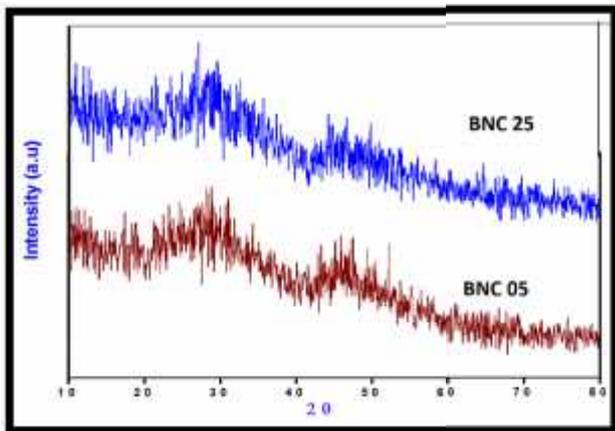


Fig. 2 X-ray diffractogram of BNC 05 and BNC 20 glasses

FTIR study

The FTIR spectra of the glasses under investigation are recorded at 303 K in the frequency range between 400 and 4000 cm⁻¹ as shown in Fig 3. The spectrum is found to exhibit few absorption peaks which can be categorized as sharp, medium and broad. The spectra provide an insight into the interaction between the cadmium, sodium and the boron trioxide. Generally, the FTIR spectra of B₂O₃ consist of BO₃, BO₄ and boroxol ring. The characteristic band (at 806 cm⁻¹) of

vitreous B₂O₃ is assigned to the symmetric stretching vibration of the boroxol ring. The peak at 806 cm⁻¹ is found missing in the spectra of BNC glasses, which indicates the absence of boroxol ring in the glass network.

The observed band around 1003 cm⁻¹ is due to asymmetric stretching vibrations of the B-O bonds in BO₄ units [11] whereas the band at 1352 cm⁻¹ is attributed to the B-O bonds due to stretching vibrations of trigonal BO₃ units [13,13] in the borate network. The additional band around 710 cm⁻¹ is due to the bending vibration of B-O-B linkage. The bands in the region 400-470 cm⁻¹ are assigned to the vibration of the metal cation [14]. In the present spectra, the band around 470 cm⁻¹ is due the vibration of metal cation Cd²⁺ [15,16]. The addition of cadmium oxide makes an increase in the intensity of vibrational band due to BO₄ group at the expense of BO₃ group, indicating increase in the compactness of the glass network.

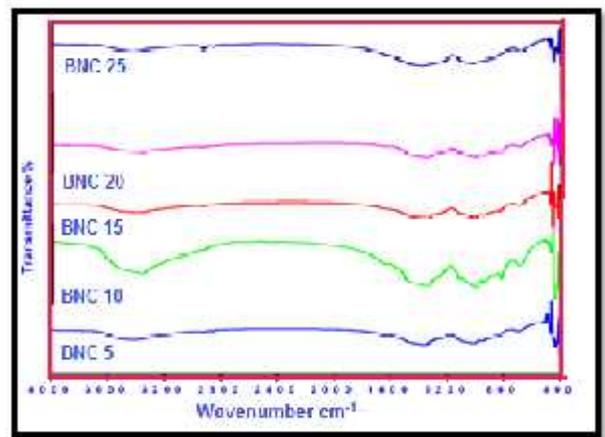


Fig. 3 FTIR spectra for BNC glasses

Table 2 Band positions and their corresponding assignments of infrared spectra of BNC glasses

Wavenumber cm ⁻¹	Assignment
~1003	B-O stretching vibrations of the tetrahedral BO ₄
~1352	B-O stretching vibrations of the trigonal BO ₃ unit
~710	Bending vibrations of B-O-B linkages
~470	Vibration of metal cation Cd ²⁺

Thermal Studies

DTA is a thermal analysis technique that tells about the behavior of glass systems under various temperatures ranges and gives an idea about the structural changes in the network on addition of the modifiers oxide. The glass transition temperature T_g is identified as endothermic peak, followed by T_c an exothermic peak which is pronounced as glass crystallization temperature. These two peaks are followed by another endothermic peak, identified as glass melting temperature T_m. Fig 4 shows the DTA curve for all prepared glass samples.

In the BNC glasses, T_g, T_c, and T_m values increase from 143°C to 313 °C, 238 °C to 515 °C and 475 °C to 798 °C with the substitution of CdO content at the expense of Na₂O content respectively. The increase in T_g, T_c and T_m values implies that the number of bridging oxygen groups increase and the results in the formation B-O-Cd bonds instead of B-O-B and B-O-Na

bonds. Besides, the incorporation of CdO into BNC glass network will change the borate structure by creating BO_4 units at the expense of BO_3 units. Hurby's parameter (K_{g1}) gives the information on the stability of the glass against devitrification. The values of S and K_{g1} increase with increasing cadmium ion concentration. This is due to the formation of BO_4 units which increases the stability of the glass [17]. And the large value of S implies better thermal stability of super cooled liquid [18].

Table 3 Physical properties of B_2O_3 - Na_2O -CdO glasses

Parameters	BNC 5	BNC10	BNC15	BNC20	BNC25
Glass transition temperature ($^{\circ}\text{C}$)	143	150	297	304	313
Crystallization temperature ($^{\circ}\text{C}$)	238	299	456	483	515
Melting temperature ($^{\circ}\text{C}$)	475	560	720	754	798
Thermal stability (S)	237	261	264	271	283
Hruby's parameter (K_{g1})	0.40	0.57	0.60	0.66	0.71

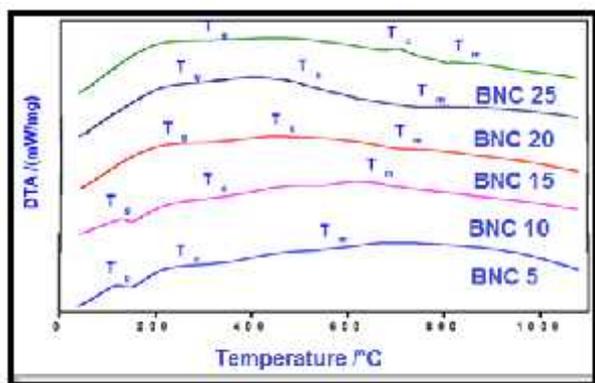


Fig.4 DTA curves of BNC glasses

CONCLUSION

Sodium borate glasses with compositions $70\text{B}_2\text{O}_3$ - $(30-x)\text{Na}_2\text{O}$ -CdO have been successfully prepared by melt quenching technique. Presence of broad band in XRD patterns demonstrates amorphous nature of glass samples. The FTIR spectra confirmed the existence of trigonal and tetrahedral borate groups with an establishment of B-O-Cd bonds. The glassy state of the sample is characterized using DTA measurements. Further, the increasing behavior of T_g , T_c , and T_m , S and K_{g1} indicates the increasing strength of the investigated glasses against diversification.

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