International Journal of Advance Research in Science and Engineering
Volume No 06, Special Issue No. 03, September 2017, AFM-2017
www.ijarse.com
IJARSE
ISSN: 2319-8354

STRUCTURAL AND DIELECTRIC STUDIES OF COPPER DOPED ZINC BORATE GLASS CERAMIC SYSTEM

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Abstract

Transparent (40-x) ZnO- xCuO - $60B_2O_3$ (x = 0,10 mol %) glasses have been prepared via melt- quenching technique and converted to glass ceramics by controlled crystallization. The structural characterization has been done using X-ray Powder Diffraction and Fourier Transform- Infrared (FT-IR) spectra. The dielectric constant of the glass ceramics are studied as a function of frequency using an LCR meter. The ZnB_4O_7 and $Zn_4O(B_6O_{12})$ crystalline phases are identified from XRD. The FT-IR studies show that the glass ceramics are made of [BO_4] and [BO_3] structural units. The dielectric analysis shows that the dielectric constant decreases with the content of CuO.

Keywords: Glass ceramics, crystalline phases, Conductivity, Nonbridging oxygen

1. Introduction

Zinc borate is a multifunctional fire retardant and synthetic hydrate metal borate containing different proportion of zinc and boric oxides [1]. It is an important green material that can be used to remove various toxic gases and organic compounds and can be synthesized in an environmentally friendly manner. Many methods have been developed for the synthesis of zinc borates (ZnB_4O_7, $Zn_8[(BO_3)_3O_2(OH)_3]$, $Zn_2B_6O_{11}\cdot 7H_2O$,$4ZnO\cdot B_2O_3\cdot$ H2O, $Zn_3B_{10}O_{18}\cdot 14H_2O$, $2ZnO.3B_2O_3\cdot 3.5H_2O$ and $2ZnO.3B_2O_3\cdot 3H_2O$) [2-4]. Xue et al. [5] and Ji et al. [6] have studied the $ZnO–B_2O_3$ binary system and found three compounds such as $Zn_3B_2O_6$, $Zn_4B_6O_{13}$ and ZnB_4O_7 with similar lattice parameters. [7]. Huppertz et al on high pressure studies synthesized the β-ZnB_4O_7, which crystallizes in the orthorhombic space group

Cmcm [8].

Pascuta et al [9] reported that when Fe_2O_3 greater than 20 mol% is added to xFe_2O_3 - 40ZnO-(60-x)B_2O_3 glass, it crystallizes in the cubic crystal system, $ZnFe_2O_4$. In the present work we made an attempt to prepare the xCuO - 40 ZnO- (60-x)B_2O_3 glass ceramics by controlled crystallization method and studied the structural and dielectric properties of glass ceramics.

2. Experimental Procedure

2.1 Sample Preparation

The glass systems (40-x) ZnO. $60B_2O_3$. xCuO (x = 0, 5, 10 mol %) were prepared by normal melt-quench technique from analytical grade chemicals of ZnO, B_2O_3 and CuO. Appropriate amounts of these chemicals were mixed in agate mortar and then melted in porcelain crucible at 1200^oC for one hour using an electric muffle furnace. The mixture was shaken frequently to ensure homogeneity. The melt was then poured into a preheated brass mold and annealed near the glass transition temperature in order to eliminate internal mechanical stresses. Finally, we get the colorless, greenish transparent glass samples. These transparent glass samples were heat treated at temperature 775^0C for crystallizing the glasses with heating rate 2^0C/min and cooling rate 1^0C/min.

2.2 Characterization of the samples

a) XRD Analysis

X-ray diffraction patterns were collected with Philips X'Pert Pro diffractometer using Cu K_α radiations (1.54056 Å) at a scan rate of 0.050 2θ s^{-1}.

b) IR spectroscopic measurements

The Fourier transform infrared (FT-IR) transmission spectra were recorded in the region 400-4000 cm^{-1} by a Shimadzu FT-IR spectrometer (Shimadzu FT-IR spectrometer, Japan), employing the KBr pellet technique.

c) Dielectric measurement

For the measurement of dielectric properties of the samples, silver paste was used as electrode material. The measurements were made at room temperature in the frequency range 1 KHz to 10 MHz using an LCR meter.

3. Results and Discussions

3.1. X-ray Diffraction

The XRD patterns of zinc borate and copper doped zinc borate glasses annealed at 775^0C for 2hour with heating rate $2^0C/1min$ and cooling rate $1^0C/1min$ are shown in Fig. 1.The diffractogram of the transformed material of zinc borate glass (ZBGC) after crystallization process suggests the presence of microcrystallites of a single phase, shown in Fig.1. From the JCPDS files these peaks can be identified as ZnB_4O_7 (Card no: ICSD #023751), which crystallizes in the orthorhombic crystal system, with lattice parameters a=13.71nm, b=8.091nm and c=8.631nm and cell volume V=957.70 nm^3.

But the diffractogram of the copper doped zinc borate glasses of all composition after crystallization process suggests the presence of microcrystallites $Zn_4O(B_6O_{12})$ (Card no: ICSD #200670), which crystallizes in the cubic crystal system, with lattice parameters a=7.478nm and cell volume V=418.17 nm^3.

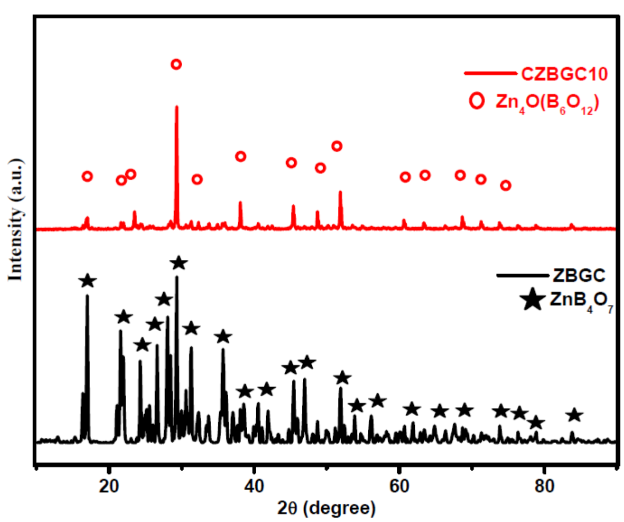


Fig.1. The XRD patterns of (40-x)ZnO-xCuO–60B_2O_3 (x = 0, 10 mol%) glass ceramics

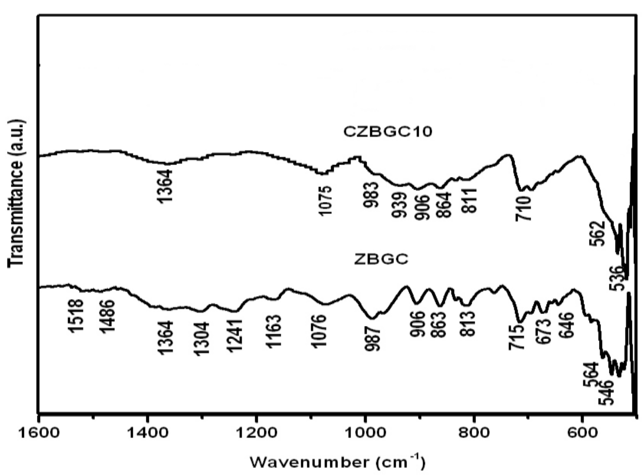
crystallized at 775^{0}C.

3.2.FT-IR spectra

The FT-IR spectrum of CZB glass ceramics under investigation in the wavenumber range 4000-400 cm^{-1} is shown in Fig. 2. The band at ~1360 cm^{-1} which are assigned to the B-O stretching vibrations of BO_3units in metaborate, pyroborate and orthoborate groups[10]. Bands which occur at 1200-1600 cm^{-1} is due to the asymmetric stretching relaxation of the B-O bonds in trigonal BO_3 units. The peak at 1075 cm^{-1} is due to the B-O stretching vibrations of B-O bonds in BO_4 units and boroxol rings. Bands which occur at 800-1200 cm^{-1} is due to the B-O bonds stretching in BO_4 units. The weak band present at 986 cm-1 is due to B-O vibration of BO_4 unit in tri, tetra and penta-borate groups. The bands at 863and 906 cm^{-1}are clear indicator of B-O bond stretching of BO_4 unit in tri,tetra and penta borates groups. The band at 811 cm^{-1} shows the existence of boroxol rings and hence consists of only BO_3 and BO_4 groups. Bands at ~710 cm^{-1}are attributed to the B-O-B bending vibrations. The band around 540cm^{-1}is attributed to the vibration of Zn^{2+}cations.The band assignments for FT-IR spectra of CZB glass ceramics are also presented in Table1. For the better identification of these bands and for the calculation of BO_4 network present in these glass networks the spectra are deconvoluted for five bands using Gaussian type function. The deconvoluted FT-IR spectrum shows that in copper doped glass ceramics the number of BO_4 network is higher than the pure zinc borate glass ceramics. This indicates that the BO_4 network is the main network builder in copper doped zinc borate glass ceramics.

Table 3.1 The assignments for FT-IR spectra of (40-x) ZnO- xCuO - 60B_2O_3 (x=0, 10mol%) glass ceramics.

$40ZnO$-$60B_2O_3$ Glass ceramics	$30ZnO$-$60B_2O_3$-$10CuO$ Glass ceramics	
ZBGC	CZBGC10	Assignments
1364	1364	B-O stretching vibrations of BO_3 units in metaborate, Pyroborate and ortoborate groups
1076`	1075	B-O strtching vibration of B-O bond of BO_4 units from boroxol rings
987	983	B-O stretching vibrations of BO_4 units in tri,tetra and pentaborate groups
906	906	B-O bond stretching of BO_4 unit in tri,tetra and penta borates groups
813	811	Boroxol rings
715	710	B-O-B bending vibrations
673	676	B-O-B bending vibrations
564	562	Zn-O Stretching vibrations



International Journal of Advance Research in Science and Engineering
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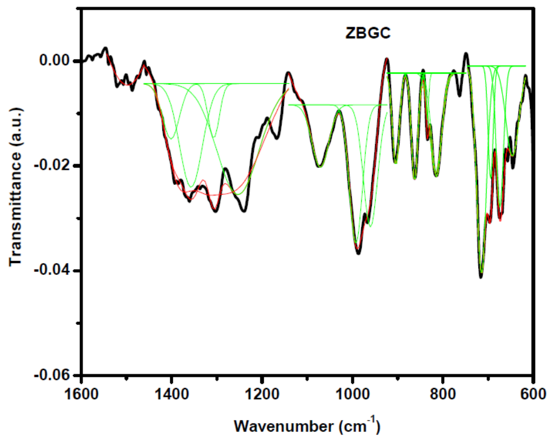
www.ijarse.com
IJARSE
ISSN: 2319-8354

Fig.2. The FT-IR spectra of (40-x) ZnO- xCuO - $60B_2O_3$ (x=0, 10mol%) glass ceramics crystallized at 775^0C.



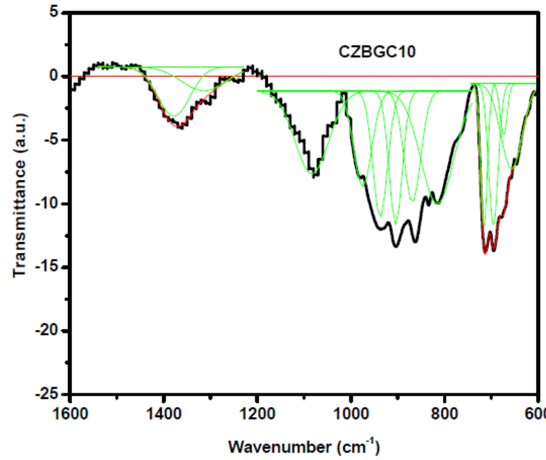
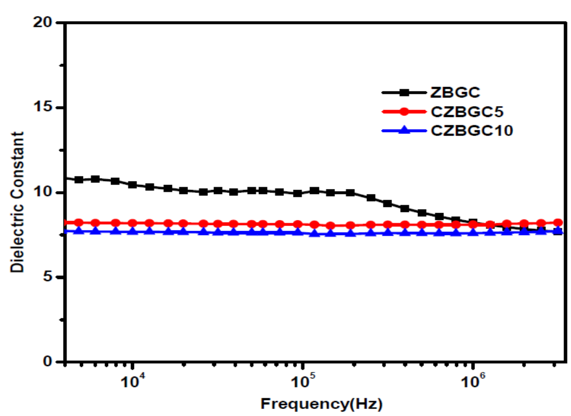


Fig.3.a. The Deconvoluted FT-IR spectra of 40 ZnO- $60B_2O_3$ glass ceramics crystallized at 775^0C.

Fig.3.b. The Deconvoluted FT-IR spectra of 30 ZnO- 10CuO- $60B_2O_3$ glass ceramics crystallized at 775^0C.

c) Dielectric Analysis



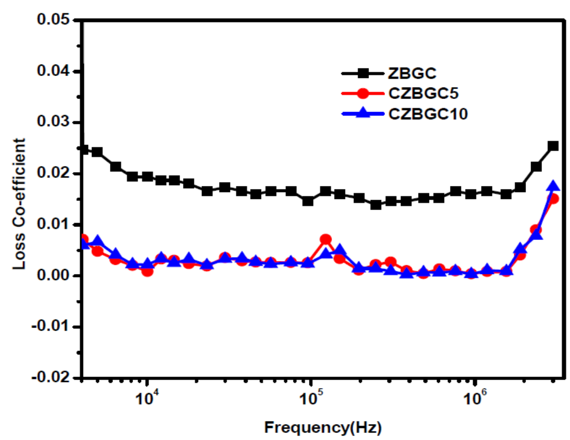


Fig.4.a.The Dielectric studies of 40 ZnO- $60B_2O_3$ glass ceramics ceramics crystallized at 775^0C.

Fig.4.b. The Loss co-efficient of 30 ZnO- 10CuO- $60B_2O_3$ glass crystallized at 775^0C.

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Fig. 4.a. and 4.b. show the variation of the dielectric constant ε_r' and dielectric loss factor tanδ measured as a function of frequency from 1 kHz to 10 MHz at room temperature. The dielectric constant ε_r' of the studied glass ceramics decreases with the addition of CuO. At 1GHz, the dielectric constant of ZBGC is 8.22, CZBGC5 is 8.1 and that of CZBGC10 is 7.6. This dielectric constant value is almost same in the entire range of studied frequencies.

The dielectric loss factor tanδ decreases with the content of CuO. This confirm the presence of BO_4 networks and decrease in the amount of non bridging oxygens(NBOs).

4. Conclusions

Transparent (40-x) ZnO- xCuO - $60B_2O_3$ ($0 \leq x \leq 10$ mol %) glasses were prepared via melt-quenching technique and converted to glass ceramics by controlled thermal treatment. The as prepared samples are characterized using X-ray Powder Diffraction and FT-IR spectra. The dielectric properties glass ceramics are studied as a function of frequency. The X-ray Diffraction analysis shows the formation of ZnB_4O_7 and $Zn_4O(B_6O_{12})$ crystals in pure and Cu doped glass ceramic samples. The FT-IR studies showed that these glasses and glass ceramics were made of [BO_4] and [BO_3] structural units and [BO_4] structural units increases with the content of CuO. The dielectric constant decreases with CuO.

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12. than ZnO, that results in the formation of excess free volume, which increases the molar volume of glasses. This helps the rotation of dipoles, which increases the dielectric loss factor tanδ.