

Effect of NiO on crystallization and structure of (40-x) ZnO- 60B₂O₃ glass system

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ABSTRACT

Transparent (40-x) ZnO- xNiO - 60B₂O₃ (0 < x < 20 mol %) glasses were prepared via melt-quenching technique and converted to glass ceramics by thermal treatment. The Ni_{1.5}Zn_{0.5} (B₂O₅) phase was identified from X-ray Powder Diffraction pattern and comparative study of structural investigations of glasses and glass ceramics were done using the Fourier Transform-Infrared spectra.

KEY WORDS: Glass ceramics, crystalline phases, X-ray Powder Diffraction pattern, Fourier Transform-Infrared spectra.

1. INTRODUCTION

ZnO based glasses have special applications in the area of varistors, dielectric layers and transparent dielectric and barrier ribs in plasma display panels (Bale et al., 2008). Among them zinc borate glasses exhibit low melting temperatures. Hence they are of technological interest owing to their applications in different fields of electronic products (Sumalatha, 2011). NiO belongs to the intermediate class of glass forming oxides could enhance the glass formation even in the less range of B₂O₃. Xue (2008) and Ji (2008) have been found three compounds: Zn₃B₂O₆, Zn₄B₆O₁₃ and ZnB₄O₇ in the binary ZnO– B₂O₃ system (Zhan, 2009). In both β-ZnB₄O₇ and β-CaB₄O₇, three BO₄ tetrahedra are combined to create the OB₃ group and to form a rather rare structure type, which was first described several years ago by the aim of high-pressure/high-temperature syntheses (Kindl, 2013). Prepared the isotypical transitional metal oxide phases like β-ZnB₄O₇, β-MnB₄O₇, β-NiB₄O₇, β-CuB₄O₇ etc and studied the structural properties. Besides these groups he also prepared many phases of NiO and studied their properties.

In this work, an attempt has been made for the preparation along with their structural characteristics of (40-x) ZnO- xNiO - 60 B₂O₃ (0 < x < 20 mol %) glasses and glass ceramics.

2. EXPERIMENTAL PROCEDURE

The glass systems (40-x)ZnO-xNiO-60 B₂O₃ with x=0, 10, 20 mol% (named as ZB, NZB10, NZB20 for glasses and ZBGC, NZBGC10, NZBGC20 for glass ceramics) were prepared by normal melt-quench technique from analytical grade chemicals of ZnO, B₂O₃ and NiO (Aldrich, 99.9% Purity). Appropriate amounts of these chemicals were mixed in agate mortar and then melted in porcelain crucible at 1200°C for one hour using an electric muffle furnace. 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 colourless glass for 40ZnO- 60 B₂O₃, reddish brown for NiO doped 40ZnO- 60 B₂O₃ glasses These transparent glass samples were heat treated at temperature 775°C for crystallizing the glasses with heating rate 20C/min and cooling rate 10C/min. This crystallization temperature is chosen on the basis of earlier reported data given (Pascuta, 2011) for the sample 40ZnO- 60 B₂O₃. 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 2 θ s⁻¹. 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).

3. RESULTS AND DISCUSSIONS

The X-ray diffraction patterns of the NZB glass samples exhibit a broad diffuse scattering at low angles instead of crystalline peaks, confirming a long range structural disorder characteristic of amorphous network. The glassy state was confirmed by the absence of peaks in the X-ray diffraction pattern. The XRD patterns of zinc borate glass and manganese doped zinc borate glasses annealed at 775°C for 2hour with heating rate 20C/1min and cooling rate 10C/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 ZnB₄O₇ (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=957.70nm³. The crystallization of zinc borate glass may be one of the effective methods for the formation of ZnB₄O₇ crystal. But the diffractogram of the transformed material of nickel doped zinc borate glasses of all composition after crystallization process suggests the presence of microcrystallites of

an identical crystalline phase regardless the NiO content. These peaks can be identified as Ni_{1.5}Zn_{0.5}(B₂O₅) (ICDD Card no: ICSD #401953), which crystallizes in the primitive crystal system, with lattice parameters a=3.312nm, b=6.138nm and c=9.222nm and cell volume V=181.71.

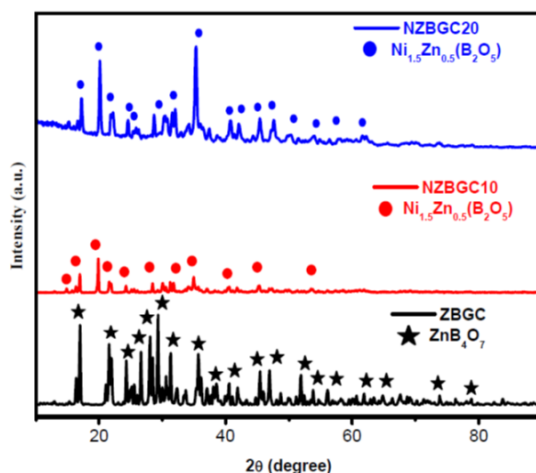


Fig.1. The XRD pattern of the xNiO – (40-x) ZnO- 60B₂O₃ (x=0, 10, 20; mol%) glass ceramics crystallized at 775^oC

3.1. FT-IR spectra: The FT-IR absorption bands of vitreous B₂O₃ are at ~720 cm⁻¹, ~1260 cm⁻¹ and ~1420 cm⁻¹, which are attributed to the B-O bond vibrations in BO₃ units. Generally, the vibrational modes of the borate glass network consist of three infrared spectral regions. The first group of bands which occur at 1200-1600 cm⁻¹ is due to the asymmetric stretching relaxation of the B-O bonds in trigonal BO₃ units, the second group which lies between 800-1200 cm⁻¹ is due to the B-O bonds stretching in BO₄ units and the third group observed around 700 cm⁻¹ is due to bending of B-O-B linkage in the borate network (Inoue, 2008).

The FT-IR spectrum of NZB glasses and glass ceramics under investigation in the wavenumber range 1600-600 cm⁻¹ is shown in Fig. 2.a and b. The band at ~1360 cm⁻¹ which are assigned to the B-O stretching vibrations of BO₃ units in metaborate, pyroborate and orthoborate groups. The peak at 975 cm⁻¹ is due to the B-O stretching vibrations of B-O bonds in BO₄ units and boroxol rings. Bands which occur at 800-1200 cm⁻¹ is due to the B-O bonds stretching in BO₄ units. Bands at ~680 cm⁻¹ are attributed to the B-O-B bending vibrations. The band around 530 cm⁻¹ is attributed to the vibration of Zn²⁺ cations. The band assignments for FT-IR spectra of NZB glasses are also presented in Table 1.

Table.1. The assignments for FT-IR spectra of xNiO – (40-x) ZnO- 60B₂O₃ (x=0, 10, 20; mol%) glasses and glass ceramics

ZB	NZB10	NZB20	ZBGC	NZBGC10	NZBGC20	Assignments
1361	1353	1353	1364	1360	1360	B-O stretching vibrations of BO ₃ units in metaborate, Pyroborate and ortoborate groups
1239	1220	1224	1241	1269	1261	Stretching vibrations of the B-O bonds of trigonal BO ₃ units
			1076	1067	1060	B-O strctching vibration of B-O bond of BO ₄ units from boroxol rings
960	973	983	987	988	986	B-O stretching vibrations of BO ₄ units in tri,tetra and pentaborate groups
680	666	672	673	698	692	B-O-B bending vibrations

The band located at ~522cm⁻¹ is due to the vibrations of ZnO₄ structural units (Prasad, 2011). The band around 700 cm⁻¹ is due to the bending of B-O-B linkage in the borate networks. All glasses show this peak around ~670 cm⁻¹. The pure ZB glass shows peaks at ~680 cm⁻¹. But the addition of NiO the peaks shifts to less wave number region ie ~670 cm⁻¹. The shifting of frequency bands from higher to lower wave number is due to the formation of nonbridging oxygens. The borate network in between 800-1200 cm⁻¹ is due to the B-O bond stretching of the tetrahedral BO₄ structural units. The band ~960 cm⁻¹ is also due to the same band in our present study. By the addition of NiO the band increases from lower to higher wavenumber range ie 973 cm⁻¹, 983 cm⁻¹ NZB10, NZB20 glasses respectively. This shows the deformation of NBOs. The borate network in

between 1200-1600 cm^{-1} is due to the asymmetric stretching relaxation of B-O bond of the trigonal BO_3 structural units. In ZB glass this band is present at $\sim 1361 \text{ cm}^{-1}$. By the addition of NiO this band shifts to lower wavenumber region, in NZB10 and NZB20 glasses ie at 1353 cm^{-1} in both glasses.

The FT-IR spectra of $(40-x) \text{ ZnO} \cdot 60\text{B}_2\text{O}_3 \cdot x\text{NiO}$ glass ceramic systems with various contents of NiO consisting of broad peaks and shoulders are presented in Fig.2.b. The band located at $\sim 522 \text{ cm}^{-1}$ is also due to the vibrations of ZnO_4 structural units. The band around 700 cm^{-1} is due to the bending of B-O-B linkage in the borate networks. Instead of a broad peak in glasses, glass ceramics show small bands. All glasses show this peak around $\sim 670 \text{ cm}^{-1}$. The pure ZB glass shows peaks at $\sim 680 \text{ cm}^{-1}$. But the crystallization of glasses the broad band in the ZB glass splits into four small bands and the NiO added glass these band splits into three small bands. The borate network in between $800\text{-}1200 \text{ cm}^{-1}$ is due to the B-O bond stretching of the tetrahedral BO_4 structural units. In the case of glasses a broad band $\sim 970 \text{ cm}^{-1}$ is seen. But in glass ceramics six peaks present at $\sim 815 \text{ cm}^{-1}$, $\sim 865 \text{ cm}^{-1}$, $\sim 906 \text{ cm}^{-1}$, $\sim 987 \text{ cm}^{-1}$, $\sim 1070 \text{ cm}^{-1}$ and $\sim 1163 \text{ cm}^{-1}$. This shows the deformation of NBOs. The borate network in between $1200\text{-}1600 \text{ cm}^{-1}$ is due to the asymmetric stretching relaxation of B-O bond of the trigonal BO_3 structural units. In glasses this band is present at $\sim 1361 \text{ cm}^{-1}$. But the crystallization of glasses the broad band in the ZB glass splits into four small bands and the NiO added glass these band splits into three small bands. This indicates that by the addition of NiO the BO_4 structural units increases and the amount of non bridging oxygen that helps to charge transport are decreases.

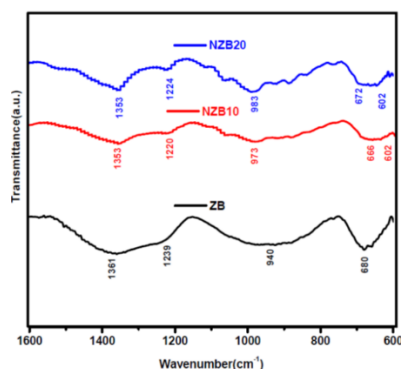


Fig.2a. The FT-IR spectra of the the $x\text{NiO} - (40-x)\text{ZnO} - 60\text{B}_2\text{O}_3$ ($x=0, 10, 20$; mol%) glasses

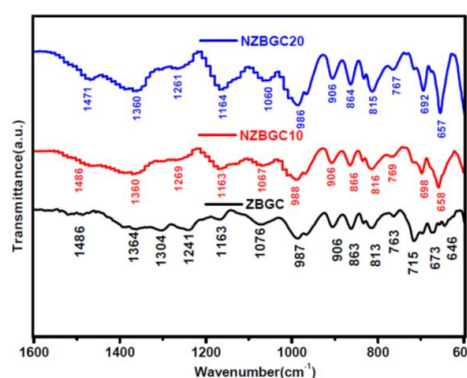


Fig.2b. The FT-IR spectra of the the $x\text{NiO} - (40-x)\text{ZnO} - 60\text{B}_2\text{O}_3$ ($x=0, 10, 20$; mol%) glass ceramics crystallized at 775°C

4. CONCLUSIONS

Transparent $(40-x) \text{ ZnO} - x\text{NiO} - 60\text{B}_2\text{O}_3$ ($0 \leq x \leq 20$ mol %) glasses were prepared via melt-quenching technique and converted to glass ceramics by thermal treatment. The phase identification was done from X-ray Powder Diffraction pattern and comparative study of structural investigations of glasses and glass ceramics were done using the Fourier Transform-Infrared spectra. The X-ray Powder Diffraction pattern indicates that ZnB_4O_7 phase with crystalline volume $V = 957.70 \text{ nm}^3$ was formed by the crystallization of zinc borate glass and $\text{Ni}_{1.5}\text{Zn}_{0.5}(\text{B}_2\text{O}_5)$ phase with crystalline volume $V = 181.71 \text{ nm}^3$ was formed by the crystallization of NiO added zinc borate glasses. The Fourier Transform-Infrared spectra indicate that with the addition of NiO the BO_4 structural units increases and the amount of non-bridging oxygen that helps to charge transport are decreases.

REFERENCES

- Bale S, Rahman S, Awasthi A.M, Sathe V, Role of Bi_2O_3 content on physical, optical and vibrational studies in $\text{Bi}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3$ glasses, J. Alloys & Comps., 460, 2008, 699.
- Bale S, Rao N.S, Rahman S, Spectroscopic studies of $\text{Bi}_2\text{O}_3\text{-Li}_2\text{O-ZnO-B}_2\text{O}_3$ glasses, Solid State Sci., 10, 2008, 326.
- Inoue T, Honma T, Dimitrov V, Komatsu T, Approach to thermal properties and electronic polarizability from average single bond strength in $\text{ZnOBi}_2\text{O}_3\text{B}_2\text{O}_3$ glasses, J. Solid state chem., 183, 2010, 3078.
- Ji L.N, Phase relations and flux research for ZnO crystal growth in the $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ system, J. Alloys & Comps., 459, 2008, 481.

Kaindl R, Sohr G, Huppertz H, Experimental determinations and quantum-chemical calculations of the vibrational spectra of β -ZnB₄O₇ and β -CaB₄O₇, Spectrochim. Acta Part A: Molecular and Biomolecular Spectroscopy, 116, 2013, 408.

Pascuta P, Culea E, Structural and thermal properties of some zinc borate glasses containing gadolinium ions, J. Mater Sci: Mater Electron, 22, 2011, 1060.

Siva Prasad Y.D, Veerabhadra Rao A, Srikanth K, Emmanuel K.A, Spectroscopic and magnetic properties as probe in the structural study of PbO-ZnO- B₂O₃ glass system doped with MnO, Rasayan, J. Chem., 4(2), 2011, 358.

Sumulatha B, Omkaram I, Rajavardhana Rao T, Linga Raju Ch, Alkaline earth zinc borate glasses doped with Cu²⁺ ions studied by EPR, optical and IR techniques, J. Non-Cryst. Solids, 357, 2011, 3143.

Xue L.P, Lin Z, Chen D.G, Huang F, Liang J.K, Subsolidus phase relations in the ZnO-MoO₃-B₂O₃, ZnO-MoO₃-WO₃ and ZnO-WO₃-B₂O₃ ternary systems, J. Alloys & Compds, 458, 2008, 144.

Zhibing Zhan, Dagui Chen, Peiwen Lv, Demin Liu, Fengbo Yan, Xianzhi Chen, Feng Huang, Sub solidus phase relations in the system ZnO-B₂O₃-V₂O₅, J. Alloys & Compds., 475, 2009, 122.