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Optical properties and crystallization of bismuth boro-tellurite glasses

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ABSTRACT

New bismuth boro-tellurite glass within the compositions $20Bi_2O_3$–$25B_2O_3$–(55–x) TeO_2–x TiO_2 ($0 \le x \le 10$ mol%) have been prepared by normal melt quenching technique. The structure of the glass and then the glass-ceramic was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and the transmission electron microscopy (TEM). The differential scanning calorimetry (DSC) measurements were carried out on the prepared glass samples to estimate their thermal behavior. Selected glass samples were heat treated at different annealing temperatures and times above the glass transition temperature. The optical absorption spectra were measured in the spectral range (380–600 nm) at room temperature. The Fourier transform infrared (FTIR) absorption spectra of all glasses were in the range (350–4000 cm^{-1}) have been recorded and designated.

1. Introduction

Boro-tellurite glasses recently used in specific applications especially in radiation shielding, microelectronics and opto–acoustics. These glasses present a favorable compromise between the requirements of low phonon energy and a relatively high thermal stability, chemical durability and the ease of fabrication [1–3]. The glasses based on heavy metal oxides (HMO) like (TeO_2, WO_3, Bi_2O_3, PbO, TiO_2, Ag_2O, etc.) have attracted attention because of their characteristic structural and physical properties. These glasses have high densities, high thermal expansion, low transformation temperatures, high refractive indices and superior infrared (IR) transmission. They appear to be among the most interesting materials for IR technologies, non-linear optics and the design of laser devices [4,5].

In addition, the glasses containing significant concentrations of transition metal oxides (TMO) such as (TiO_2, ZnO, Fe_2O_3, V_2O_5, MnO_2, etc.) are of continuing interest because of their applicability in memory switching, electrical threshold, optical switching devices, etc. [6–9].

Nano-materials (glass ceramics) are considered as key technologies for this century. Partial crystallization of the glasses with an appropriate nucleating agent is expected to influence several physical properties i.e., optical, mechanical, electrical and thermal properties in addition to the chemical durability. The transparency of the glass after the crystallization can be retained by monitoring the crystallization of a glass precursor with appropriate chemical composition and appropriate nucleating agent. Investigations along these lines have been carried out on several borates, silicate, fluoride or oxyfluoride glass systems [10–13].

The characteristics of the glass-ceramic are depending on the kind and the quantity of the crystalline phase formed as well as on the residual glass composition. Among various crystallizing agents, titanium dioxide (TiO_2) is known as a good nucleating agent [14] that can be used to precipitate micro crystals (MCs) in the glass network. Besides, TiO_2 also plays a significant role in enhancing optical nonlinearity for the empty d–orbitals of Ti^{4+} ions [15].

Previously, Bi_2O_3 – B_2O_3 –TeO_2 glasses doped with different PbO (mol%) have been prepared but the toxicity of the lead oxide was a hindrance in usage the glass in the different applications [16]. The addition of the TiO_2 to the same glass system instead of PbO enables to benefit the glass without the toxicity problem. Hasegawa et al. [17] also have been prepared the Bi_2O_3 – B_2O_3–TeO_2 glass system. This system showed high transmittance in visible and near–IR wavelengths, high refractive index, and optical non-linearity. G. Zhao et al. [18] have been studied the influence of increasing Bi_2O_3 content on the structures, thermal and optical properties of Bi_2O_3–B_2O_3–TeO_2 glasses. The results showed that the density, refractive index, and the optical basicity were increased with increasing Bi_2O_3. The Raman and photoelectron spectroscopy (XPS) spectra showed that the network of the glass mainly consists of the [TeO_4] trigonal bipyramidal, [TeO_3] trigonal pyramid, [BiO_6] octahedron, [BO_4] tetrahedron, and [BO_3] trigonal pyramid structural units. While Bi_2O_3 content increased [TeO_4] units are converted to [TeO_3] units and the coordination number around B atoms changed from 3 to 4. Bi^{5+} ions changed from 3 to 4. Bi^{5+} ions may exist in the Bi_2O_3–B_2O_3–TeO_2 glass system and their amount increase with increasing Bi_2O_3 content.

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Table 1
The values of the density (g/cm^3), molar volume (cm^3/mol) and Oxygen packing density (mol/l) of the glass studied.

Sample name	Composition (mol%)	Density (g/cm^3)	Molar volume (cm^3/mol)	Oxygen packing density (mol/l)
BBTT 0	$20Bi_2O_3–25B_2O_3–55TeO_2–0TiO_2$	5.95 ± 0.02	33.34 ± 0.09	73.50 ± 0.20
BBTT 2	$20Bi_2O_3–25B_2O_3–53TeO_2$ $2TiO_2$	5.72 ± 0.03	34.43 ± 0.17	71.17 ± 0.36
BBTT 4	$20Bi_2O_3–25B_2O_3–51TeO_2–4TiO_2$	5.53 ± 0.03	35.32 ± 0.18	69.37 ± 0.36
BBTT 6	$20Bi_2O_3–25B_2O_3–49TeO_2–6TiO_2$	5.11 ± 0.02	37.85 ± 0.13	64.73 ± 0.21
BBTT 8	$20Bi_2O_3–25B_2O_3–47TeO_2–8TiO_2$	5.00 ± 0.03	38.40 ± 0.22	63.80 ± 0.37
BBTT10	$20Bi_2O_3–25B_2O_3–45TeO_2–10TiO_2$	4.67 ± 0.01	40.76 ± 0.11	60.10 ± 0.16

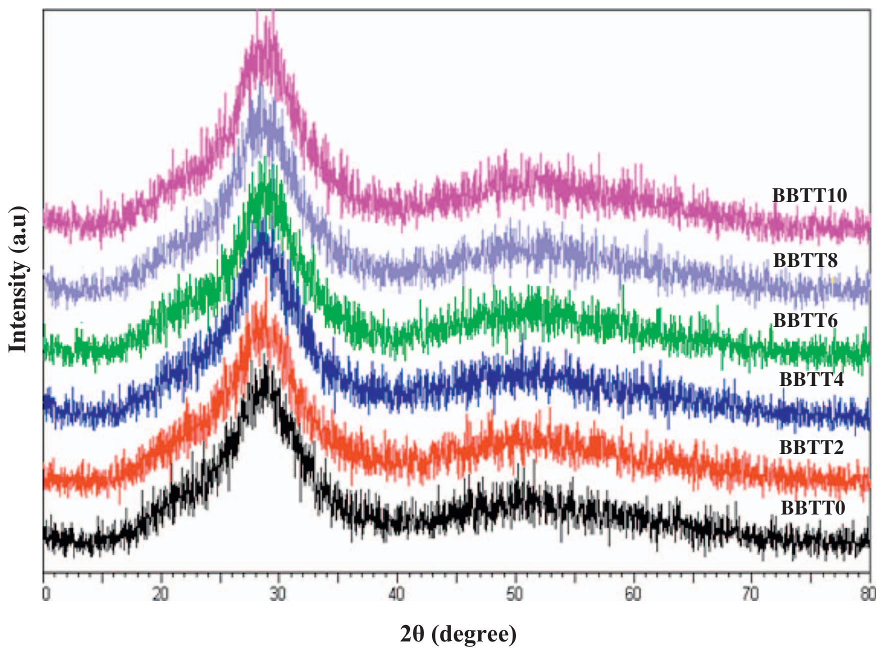

Fig. 1. X–Ray diffraction (XRD) patterns of the BBTT samples.

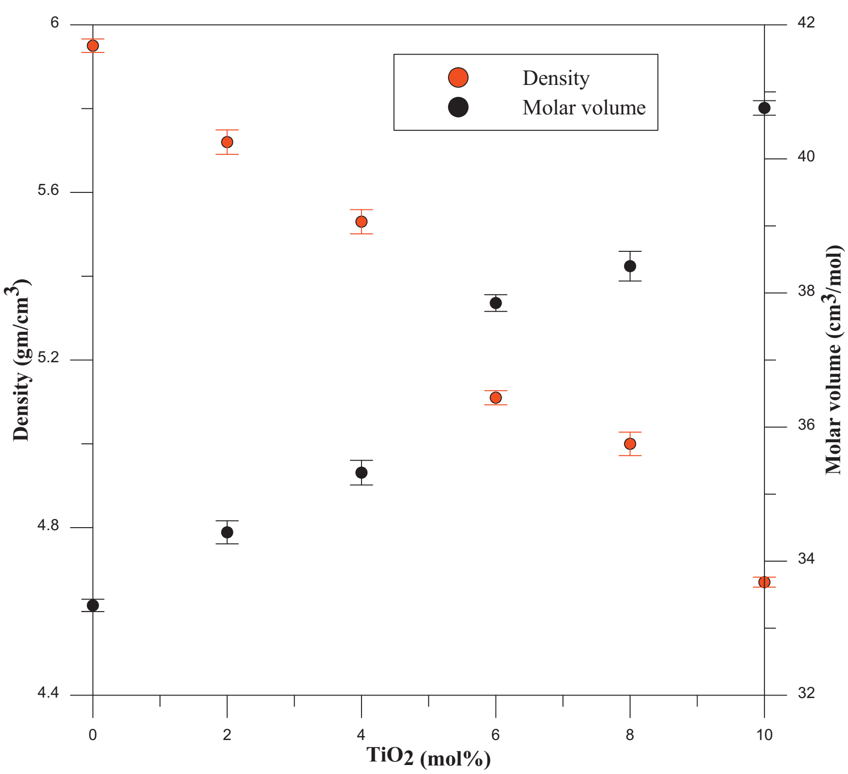

Fig. 2. Density and molar volume of the BBTT glasses as a function of TiO_2 mol%.