Original Article

Investigation on Structure of TeO$_2$-B$_2$O$_3$-SiO$_2$-Al$_2$O$_3$-KF Glasses

Phan Van Do*

Thuy Loi University, 175 Tay Son, Dong Da, Hanoi, Vietnam

Received 29 October 2019
Revised 06 November 2019; Accepted 05 March 2020

Abstract: Borotellurite glasses were prepared by melt quenching technique. Amorphous nature of samples was confirmed through X-ray diffraction (XRD) patterns. Effect of B$_2$O$_3$ content on the structure of glass network was studied through Fourier-transform infrared spectroscopy (FTIR) spectra. Optical band gap and Urbach energy were found from analysis of optical absorption spectra. Thermal studies were carried out by using Differential thermal analyzer (DTA) measurements.

1. Introduction

In recent decades, there has been an increasing attraction in synthesis and studies of structural and physical properties of heavy metal oxide glasses due to their diversity applications in optical field [1-3]. Among these glasses, tellurite glasses are technologically and scientifically important due to their outstanding properties such as low phonon energy, high refractive index, high dielectric constant, good infrared transmittance, low glass transition and melting temperature, thermal and chemical stability and high crystallization resistance [4-6]. Because of these features, tellurite glasses have become the promising materials for practical applications such as laser, upconversion, optical data storage, sensors and wave guide, etc [5-7]. However, due to the recrystallization of TeO$_2$ the pure tellurium oxide glasses can not be successfully fabricated by using the traditional melting method. Brady [4] has shown that adding more than 10 % modifiers like Na$_2$O, Al$_2$O$_3$, K$_2$O or B$_2$O$_3$ is necessary to avoid recrystallization when the TeO$_2$ glass is fabricated by using a general glass making process. It is noted that boric oxide (B$_2$O$_3$) is one of the representative glass forming oxides and flux material [7]. In

*Corresponding author.
Email address: phanvando@tlu.edu.vn
https://doi.org/10.25073/2588-1124/vnumap.4425
TeO$_2$-B$_2$O$_3$ glasses, borate not only acts as a former but also as a modifier [2, 3]. The presence of B$_2$O$_3$ component has reduced the melting temperature of glasses and increased RE$^{3+}$ ions solubility [3, 7]. Thus, these materials have taken the advantages of both tellurite and borate hosts. So far, there have been many reports on optical properties of rare earth and transition metal doped TeO$_2$-B$_2$O$_3$ glasses [1-3, 5-7]. However, to the best of our knowledge, there have been only limited investigations on structural properties of the borotellurite glasses. In this work, we focused on studying the influence of B$_2$O$_3$ concentration on structure of borotellurite glass with components of B$_2$O$_3$, TeO$_2$, Al$_2$O$_3$, SiO$_2$ and KF.

2. Experimental

Borotellurite glasses with compositions of $x$B$_2$O$_3$-(80- $x$)TeO$_2$-5Al$_2$O$_3$-10SiO$_2$-5KF, where $x$ = 30 and 50, was prepared by melt quenching technique. The samples are denoted by B3Te5 and B5Te3, respectively. The starting mixed powder was grinded in an agate mortar and melted in an electric furnace at 1250 °C for 1 h in a cover platinum crucible. The liquids were poured into reheated copper plate and pressed with another copper plate so that the glassy samples in the form of discs were obtained. The obtained glass samples were subsequently annealed at 400 °C for 6 h, after that they were slowly cooled down to room temperature. This annealing process was made to avoid the undesirable thermal strain. For optical measurements, the glass samples were sliced and polished to get a uniform thickness of 2 mm. Absorption spectra were carried out using Cary 5E (Varian Instruments, Sugar lane, Tex) in the wavelength region 200-500 nm with a spectra resolution of 1.0 nm. The amorphous nature of the prepared samples was ascertained from X-ray powder diffraction using Cu-K$_{α}$ radiation (D8 ADVANCE-Brucker). The FTIR spectra in range of 400-4000 cm$^{-1}$ were measured on JASCO-FT/IR 6300 spectrophotometer with 4 cm$^{-1}$ resolution. Differential thermal analyzer (DTA) measurement was carried out on the NETZSCH STA-409 PC/PG equipment. All measurements were carried out at room temperature.

3. Results and Discussion

3.1. X-ray Diffraction (XRD) Pattern

![Fig. 1. XRD patterns of borotellurite glasses.](image_url)
The XRD patterns of the prepared glasses, which are presented in Fig. 1, show an intense diffraction band at $2\theta$ angle about 23° and two weaker bands at 43 and 66°. There are no sharp peaks resulting from crystalline phase in the XRD curve. Consequently, it is suggested that the obtained glasses are amorphous materials [1, 8].

3.2. Fourier-transform Infrared (FTIR) Spectra

IR absorption spectra of the borotellurite glasses measured from 400 cm$^{-1}$ to 4000 cm$^{-1}$ are shown in Fig.2. The peak positions and their assignments are presented in Table 1. It can be seen that the FTIR spectra of the prepared glasses include absorption bands in three main regions 400-880 cm$^{-1}$, 880-1700 cm$^{-1}$ and 2000-3500 cm$^{-1}$. These bands are the characteristic absorption bands of tellurite network, borate network and water molecule, respectively [3, 8].

As shown in Fig. 2, the IR absorption region of tellurite network includes two clear peaks at 472 and 686 cm$^{-1}$ and a shoulder at about 860 cm$^{-1}$. The peak at 460 cm$^{-1}$ is assigned to bending vibrations of the Te-O-Te or O-T-O linkage between [TeO$_4$] groups [3, 8]. This band is clearly recorded at the concentration of 30 mol% B$_2$O$_3$ but it becomes weaker at 50 mol% concentrations. The shoulder at 860 cm$^{-1}$ has origin from the Te-O bending vibration in [TeO$_3$] and [TeO$_6$] units [3, 9].

It is well-known that borate glass network is built from [BO$_4$] and [BO$_3$] structure units, in which three [BO$_3$] groups are connected to create the boroxol rings [1]. For the B$_2$O$_3$ glasses, there is about 80% of the boron atoms present in the boroxol rings [8]. The IR absorption bands of the borate glasses are often recorded in two mainly regions to be 800-1200 cm$^{-1}$ and 1200-1700 cm$^{-1}$. These regions relate to the vibrations of [BO$_3$] and [BO$_4$] groups, respectively [3]. In our case, a broad absorption band from 930 to 1100 cm$^{-1}$ is recorded in the first region. This band is assigned to B-O-B stretching vibration of [BO$_4$] units in tri-, tetra- and pentaborate groups. In the second region, there are three bands which are recorded at energies of 1247, 1400 and 1630 cm$^{-1}$. The bands have origin from B–O stretching vibrations in [BO$_3$] units from boroxol rings, B-O stretching vibrations of BO$_3$ units in meta-, pyro-, orthoborate groups and B-O bond in isolated pyroborate group, respectively [8, 9].

In B$_2$O$_3$-TeO$_2$ glasses, the strong interaction between B$_2$O$_3$ and TeO$_2$ components can create the change in structure of glasses leading the change in position as well as the intensity of IR absorption bands. For the borotellurite glasses, the results obtained as follows: (i) the relative area ratio of [BO$_4$]
and [BO₃] units is found to decrease from 1.32 to 0.56 when the B₂O₃ content increases from 30 to 50 mol %. This indicates that when increasing B₂O₃ content the tetrahedral [BO₄] units are gradually replaced by trigonal [BO₃] units; (ii) the relative area ratio of [TeO₄] and [TeO₃]+[TeO₆] units decreases from 0.36 to 0.15. This behavior may be due to the transformation of [TeO₄] to [TeO₆] units. The transformation process from [BO₄] to [BO₃] units increases the number of non-bridging oxygen atoms would decrease the connectivity of the glass network, depolymerize of borate chains and would necessitate quite a radical rearrangement of the network formed by the [TeO₆] octahedral. These [TeO₆] groups are linked by connecting vertices instead of edge connection between [TeO₄] units. This reduces the rigidity of glass network significantly [7, 8].

| Energy  | Assignment                                      |
|---------|-------------------------------------------------|
| 3450    | Fundamental stretching of O-H group             |
| 2930    | Hydrogen bonding                                |
| 2360    | -OH group                                       |
| 1630    | B-O' bond in isolated pyroborate group          |
| 1400    | B-O stretching vibrations of BO₃ units in meta-, pyro-, and orthoborate groups |
| 1247    | B-O stretching vibrations in [BO₄] units from boroxol rings |
| 930-1100| B-O-B stretching vibration of [BO₃] units in tri-, tetra- and pentaborate groups |
| 860     | Te-O bending vibration in [TeO₅] and [TeO₆] units |
| 700     | Stretching vibrations of [TeO₄] trigonal pyramidal with non-bridging oxygen |
| 472     | Te-O-Te or O-Te-O linkage bending vibrations between two [TeO₄] groups |

3.3. Determination of Optical Band Gap and Urbach Energy

The study on absorption edge can provide useful optical information such as the optical transitions and band gap of the materials. The optical band gap (E_g) is an important parameter in order to describe the nature of the solid state laser material. The absorption spectra of borotellurite glasses are shown in Fig. 3. It can be seen that there is no sharp absorption edge which corresponds to characteristic of amorphous materials. The absorption coefficient, α(ν), near the edge of the of curve can be determined by using the following relation [3, 9]

\[ α(ν) = \frac{2.203A}{d} \]  

(1)

where d (cm) is the thickness of the sample and A corresponds to absorbance. The absorption coefficient relates to phonon energy (hv) by using the following expression [9, 10]

\[ α(ν) = \frac{B(νν - E_g)^r}{νν} \]  

(2)

with hv (eV) is phonon energy; r is the index number which is used to determine the nature of the inter band electronic transition causing the absorption with the values 1/2 and 2 correspond to direct and indirect transitions, respectively; B is the band tailing parameter and E_g is the optical band gap energy. Fig. 4 presents the curve representing the dependence of (α, hv)¹/₂ on hv for the indirect transition. The value of E_g has been obtained by extrapolating the linear region of the curves to meet at (α, hv)¹/₂ = 0. The band tailing parameter values could also be obtained through the slope of the curves of the absorption spectra at linear region. By the same method, the values of E_g and B for the direct allowed transitions have been calculated. For the B₂O₃-TeO₂ glass, the formation is not sufficient to determine whether the transitions are the direct and indirect allowed transitions. Thus, the E_g values for both two kinds of transitions have been calculated. The results are presented in Table 2.
It can be seen that there is no significant difference in values of $E_g$ between indirect and direct transition. In addition, value of $E_g$ increases with the increase of $B_2O_3$ content. The increase of $E_g$ can be due to the structural changes and the formation of greater number of non-bridging oxygens taking place in the glass network. The location of absorption edge depends on the oxygen bond strength in the glass forming network. The increase of $B_2O_3$ content would change the oxygen bonding in the glass network and the change in oxygen bonding such as the formation of non-bridging oxygen would result in the change of the absorption characteristics.

It is known that the absorption coefficient near absorption edge is given by the Urbach rule [10, 11]

$$\alpha(\nu) = \alpha_0 \exp \left( -\frac{\hbar \nu}{\Delta E} \right)$$

Equation 3 can be rewritten as follows:
where $\Delta E$ is the Urbach energy which corresponds to the width of the localized states which is used to characterize the degree of disorderness in the amorphous and crystalline materials, $\alpha_0$ is a constant. The dependence of $\ln \alpha$ on $h\nu$ is shown in the inset of Fig. 4. The Urbach energy $\Delta E$ is determined from the inverse of the slope of the curve in linear region. The value of $E_g$ and $\Delta E$ in BT glasses are in the same order as those of some boro-tellurite glasses such as $\text{B}_2\text{O}_3$-$\text{TeO}_2$-$\text{Na}_2\text{CO}_3$-$\text{NaF}$ [3], $\text{B}_2\text{O}_3$-$\text{ZnO}$-$\text{TeO}_2$ [9], $\text{TeO}_2$-$\text{B}_2\text{O}_3$-$\text{BaO}$-$\text{AF}_2$ [10] and $\text{B}_2\text{O}_3$-$\text{TeO}_2$-$\text{MgO}$-$\text{K}_2\text{O}$ [11]. It is observed from the Table 2 that the $\Delta E$ values increase with the increase in $\text{TeO}_2$ content. Maheshvaran et al [3] have reported that the materials with larger Urbach energy would have greater tendency to convert weak bonds into defects. In the boro-tellurite glasses, the TeO$_4$ units and BO$_4$ units have a strong tendency to link with each other to form BTeO$_3$ and BTeO$_5$ units, which leads to a higher connectivity in the glass network which in turn decrease the number of defects in the title glasses with low TeO$_2$ content. The increase of TeO$_2$ content leads to the increase in the number of TeO$_4$ pyramids, making the structure less stable than the borate glasses. Therefore, that results in the increase of Urbach energy.

### Table 1. Optical band gap, Urbach energy and band tailing parameter of some glasses

| Samples  | $E_{\text{ind}}$ (eV) | $B$ (cm.eV)$^{1/2}$ | $E_{\text{dir}}$ (eV) | $B$ (cm$^{-2}$.eV$^{-1}$) | $\Delta E$ (eV) |Refs |
|----------|----------------------|---------------------|----------------------|----------------------|----------------|-----|
| B3T5     | 2.82                 | 1.37                | 3.21                 | 160.4                | 0.32           | Present |
| B5T3     | 2.88                 | 1.25                | 3.28                 | 130.6                | 0.24           | Present |
| B3TN     | 2.89                 | -                   | 3.11                 | -                    | 0.54           | [3]   |
| BZT      | 2.68                 | 13.31               | -                    | -                    | 0.33           | [9]   |
| TBBFE    | 2.79                 | 25.89               | 2.89                 | 1771.4               | 0.29           | [10]  |
| BTMK     | 2.96                 | 25.41               | 3.21                 | 2631.98              | 0.39           | [11]  |

### 3.4. Thermal Studies

### Table 3. Thermal properties of some glasses

| Samples  | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $\Delta T$ (°C) | $H$ |Refs |
|----------|------------|------------|------------|----------------|-----|-----|
| B3T5     | 313        | 435        | 1048       | 122            | 0.39 | Present |
| B5T3     | 305        | 431        | 1042       | 126            | 0.41 | Present |
| 50B$_2$O$_3$.10PbO.10Al$_2$O$_3$.10ZnO.20Li$_2$O | 423        | 592        | 773        | 169            | 0.40 | [11]  |
| 75TeO$_2$.10TiO$_2$.15WO$_3$ | 370        | 436        | -          | 66             | 0.18 | [12] |
| 48B$_2$O$_3$.25Li$_2$O.25NaF.2Dy$_2$O$_3$ | 400        | 513        | -          | 113            | 0.28 | [13] |
| 60P$_2$O$_5$.20PbO.20ZnO | 278        | 372        | -          | 96             | 0.35 | [14] |

The thermodynamic properties of borotellurite glasses are analyzed by using the DTA curve in Fig. 5. From the DTA curves, the glass transition temperature ($T_g$), crystallization temperature ($T_c$) and melting point temperature ($T_m$) of samples were determined. The difference between the onset crystallization temperature and glass transition temperature, $\Delta T = T_c - T_g$, has often been considered as a measure of glass stability: the larger $\Delta T$ corresponds to the higher stability of glass gets. The glasses with a high thermal stability and a low temperature interval ($T_m - T_c$) are the promising material for optical fiber fabrication due to the small possibility of crystallization problems. Another critical parameter, which is also used to estimate the stability of glasses, is called the Hruby number. This
Parameter is defined as $H = \Delta T/T_g$. It is noted that the greater the value of the Hruby parameter, the higher the glass forming tendency and the stability for a given glass system. The results are shown in Table 2 in the comparison with those of some other hosts. It can be seen that there is a light shift of the $T_g$, $T_c$ and $T_m$ toward low temperature when increasing the concentration of $B_2O_3$. This behavior of prepared glasses may relate to the low melting point and the strong recrystallization ability of $B_2O_3$ composition. For the borotellurite glasses, the value of $\Delta T$ and $H$ parameters are equivalent to those of BPAZL [1], PPbZ [14] but are larger than those of TeTiW [12] and BLN [13]. The large values of $\Delta T$ and $H$ give a large working range during operations for fiber drawing [1, 14].

Fig. 5. DTA curve of borotellurite glass.

4. Conclusion

In borotellurite glasses with $B_2O_3$ content larger than 30 mol%, the strong interaction between $B_2O_3$ and constituent would produce the change of glass network structure. The tetrahedral [BO$_4$] units are gradually replaced by trigonal [BO$_3$] units. Consequently, the number of non-bridging oxygen atoms increase and the co-ordination of the Te atom can be changed progressively and probably the formation of [TeO$_6$] distorted octahedral. This decreases the connectivity of the glass network. The increase of $B_2O_3$ content also leads to the increase of band gap energy as well as the Hruby number. The large value of the Hruby number shows that the prepared glasses are promising materials for laser design.

Acknowledgments

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.03–2017.352

References

[1] G. Lakshminarayana, S.O. Baki, A. Lira, U. Caldiño, A.N. Meza-Rocha, I.V. Kityk, A.F. Abas, M.T. Alresheedi, M.A. Mahdi, Effect of alkali/mixed alkali metal ions on the thermal and spectral characteristics of Dy$^{3+}$-B$_2$O$_3$-PbO-Al$_2$O$_3$-ZnO glasses, J. Non-Cryst. Solids 481 (2018) 191-201.
https://doi.org/10.1016/j.jnoncrysol.2017.10.047

[2] V.P. Tuyen, V.X. Quang, P.V. Do, L.D. Thanh, N.X. Ca, V.X. Hoa, L.V. Tuat, L.A. Thi, M. Nogami, An in-depth study of the Judd-Ofelt spectroscopic properties and energy transfer of Dy$^{3+}$ in alumino-lithium-telluroborate glasses, J. Lumin 210 (2019) 435-443. https://doi.org/10.1016/j.jlumin.2019.03.009

[3] K. Maheshvaran, P.K. Veeran, K. Marimuthu, Structural and optical studies on Eu$^{3+}$ doped borotellurite glasses, Solid State Sciences 17 (2013) 54-62. https://doi.org/10.1016/j.solidstatesciences.2012.11.013

[4] G.W. Brady, Structure of Tellurium Oxide Glass, J. Chem. Phys. 27 (1957) 300-305. https://doi.org/10.1063/1.1743690

[5] S. Rada, M. Culea, E. Culea, Structure of TeO$_2$B$_2$O$_3$ glasses inferred from infrared spectroscopy and DFT calculations, J. Non-Cryst. Solids 354 (2008) 5491-5495. https://doi.org/10.1016/j.jnoncrysol.2008.09.009

[6] A.E. Ersundu, M. Celikbilek, S. Aydin, Characterization of B$_2$O$_3$ and/or WO$_3$ containing tellurite glasses, J. Non-Cryst. Solids 358 (2012) 641-647. https://doi.org/10.1016/j.jnoncrysol.2011.11.012

[7] V.P. Tuyen, B. Sengthong, V.X. Quang, P.V. Do, H.V. Tuyen, L.X. Hung, N.T. Thanh, M. Nogami, T. Hayakawa, B.T. Huy, Dy$^{3+}$ ions as optical probes for studying structure of boro-tellurite glasses, J. Lumin 178 (2016) 27-33. http://dx.doi.org/10.1016/j.jlumin.2016.05.027.

[8] D.V. Phan, V.X. Quang, H.V. Tuyen, T. Ngoc, V.P. Tuyen, L.D. Thanh, N.X. Ca, N.T. Hien, Structure, optical properties and energy transfer in potassium-aluminoborotellurite glasses doped with Eu$^{3+}$ ions, J. Lumin 216 (2019) 116748. https://doi.org/10.1016/j.jlumin.2019.116748.

[9] P.G. Pavani, K. Sadhana, V.C. Mouli, Optical, physical and structural studies of boro-zinc tellurite glasses, Physica B 406 (2011) 1242-1247. https://doi.org/10.1016/j.physb.2011.01.006

[10] S. Selvi, K. Marimuthu, G. Muralidharan, Structural, and luminescence studies of Eu$^{3+}$:TeO$_2$B$_2$O$_3$-AO$_2$F$_2$ (A = Pb, Ba, Zn, Cd, Sr) glasses, J. Mol. Struct. 1144 (2017) 290-299. DOI: 10.1016/j.molstruc.2017.05.031

[11] K.K. Maheshvaran, K. Marimuthu, Concentration dependent Eu$^{3+}$ doped boro-tellurite glasses – Structural and optical investigation, J. Lumin 132 (2012) 2259-2267. https://doi.org/10.1016/j.jlumin.2012.04.022

[12] L. Jyothi, G. Upender, R. Kuladeep, D.N. Rao, Structural, thermal, optical properties and simulation of white light of titanium-tungstate-tellurite glasses doped with dysprosium, Mater. Res. Bull. 50 (2014) 424-431. https://doi.org/10.1016/j.materresbull.2013.11.013

[13] R.T. Karunakaran, K. Marimuthu, S.S. Babu, S. Arumugam, Dysprosium doped alkali fluoroborate glasses-Thermal, structural and optical investigations, J. Lumin. 130 (2010) 1067-1070. https://doi.org/10.1016/j.jlumin.2010.01.026

[14] N. Vijaya, K.U. Kumar, C.K. Jayasankar, Dy$^{3+}$ doped zinc fluorophosphate glasses for white luminescence applications, Spectrochim. Acta, Part A 113 (2013) 145-153. https://doi.org/10.1016/j.saa.2013.04.036