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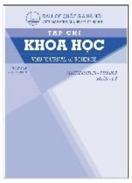

Original Article

Investigation on Structure of TeO_2-B_2O_3-SiO_2-Al_2O_3-KF Glasses

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Abstract: Borotellurite glasses were prepared by melt quenching technique. Amorphous nature of samples was confirmed through X-ray diffraction (XRD) patterns. Effect of B_2O_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, ect [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_2O, Al_2O_3, K_2O or B_2O_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_2O_3) is one of the representative glass forming oxides and flux material [7]. In

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TeO_2-B_2O_2 glasses, borate not only acts as a former but also as a modifier [2, 3]. The presence of B_2O_2 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_2O_2 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_2O_3 concentration on structure of borotellurite glass with components of B_2O_3, TeO_2, Al_2O_3, SiO_2 and KF.

2. Experimental

Borotellurite glasses with compositions of xB_2O_3-$(80-x)TeO_2$-$5Al_2O_3$-$10SiO_2$-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-Kα 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

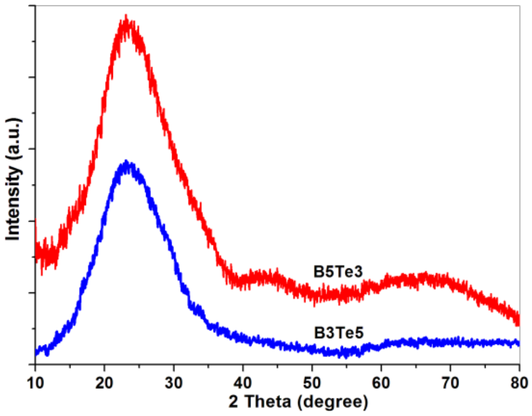

Fig. 1. XRD patterns of borotellurite glasses.

The XRD patterns of the prepared glasses,which are presented in Fig. 1, show an intense diffraction band at 2θ 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

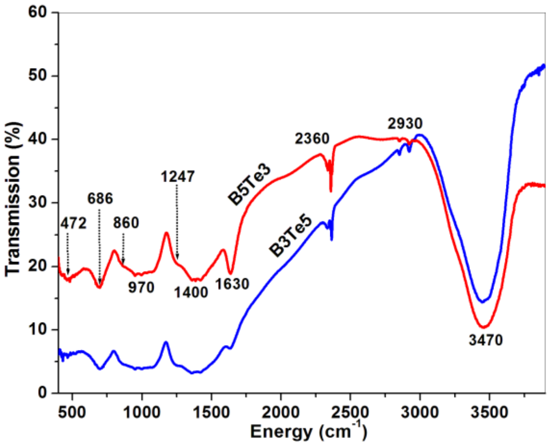

Fig. 2. FTIR spectra of borotellurite glasses.

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_2O_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_2O_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_2O_3-TeO_3 glasses, the strong interaction between B_2O_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 [BO_3] units is found to decrease from 1.32 to 0.56 when the B_3O_3 content increases from 30 to 50 mol %. This indicates that when increasing B_2O_3 content the tetrahedral [BO_4] units are gradually replaced by trigonal [BO_3] units; (ii) the relative area ratio of [TeO_4] and [TeO_3]+[TeO_6] units decreases from 0.36 to 0.15. This behavior may be due to the transformation of [TeO_4] to [TeO_6] units. The transformation process from [BO_4] to [BO_3] units increases the number of non-bridging oxygen atoms would decrease the connectivity of the glass network, depolymerize of borate chains and would necessite quite a radical rearrangement of the network formed by the [TeO_6] octahedral. These [TeO_6] groups are linked by connecting vertices instead of edge connection between [TeO_4] units. This reduces the rigidity of glass network significantly [7, 8].

Table 1. The assignment of FTIR bands in borotellurite glasses

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 BO_3 units in meta-, pyro-, and orthoborate groups
1247	B–O stretching vibrations in [BO_3] units from boroxol rings
930-1100	B-O-B stretching vibration of [BO_4] units in tri-, tetra- and pentaborate groups
860	Te-O bending vibration in [TeO_3] and [TeO_6] units
700	Stretching vibrations of [TeO_3] trigonal pyramidal with non-bridging oxygen
472	Te-O-Te or O-Te-O linkage bending vibrations between two [TeO_4] 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(v), near the edge of the of curve can be determined by using the following relation [3, 9]

$$\alpha(\nu) = \frac{2,203A}{d} \tag{1}$$

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]

$$\alpha(\nu) = \frac{B(h\nu - E_g)^r}{h\nu} \tag{2}$$

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 $(\alpha.hv)^{1/2}$ 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 $(\alpha.hv)^{1/2} = 0$. 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 B_2O_3-TeO_2 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.

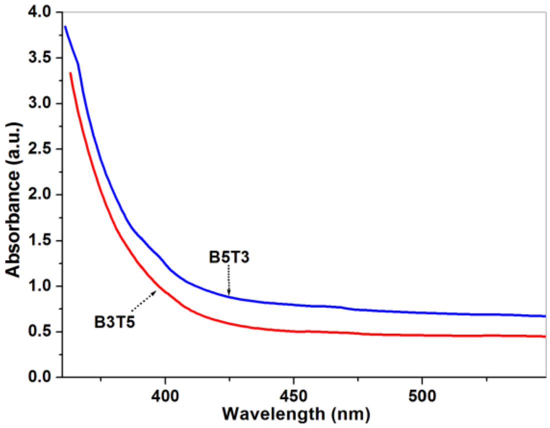

Fig. 3. Absorption spectra of borotellurite glasses.

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.

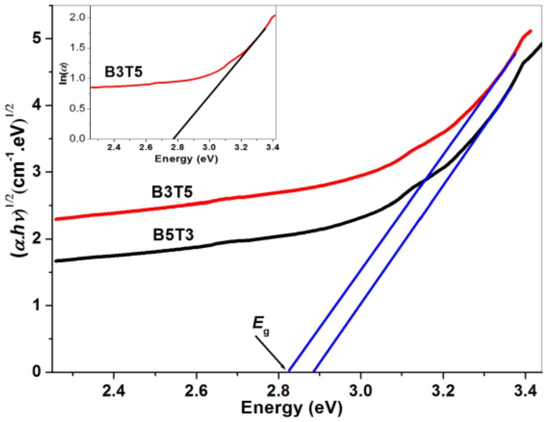

Fig. 4. The dependence of $(\alpha.h\nu)^{1/2}$ on $h\nu$ for the indirect transition.

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

$$\alpha(\nu) = \alpha_0 \exp\left\{-\frac{h\nu}{\Delta E}\right\} \tag{3}$$

Equation 3 can be rewritten as follows:

$$\ln \alpha(\nu) = \ln B - \frac{h\nu}{\Delta E} \tag{4}$$

where ΔE 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, α_0 is a constant. The dependence of $\ln\alpha(\nu)$ on $h\nu$ is shown in the inset of Fig. 4. The Urbach energy ΔE is determined from the inverse of the slope of the curve in linear region.The value of E_g and ΔE in BT glasses are in the same order as those of some boro-tellurite glasses such as B_2O_3-TeO_2-Na_2CO_3-NaF [3], B_2O_3-ZnO-TeO_2 [9], TeO_2-B_2O_3-BaO-AF_2 [10] and B_2O_3-TeO_2-MgO-K_2O [11]. It is observed from the Table 2 that the ΔE values increase with the increase in 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 borotellurite 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	Indirect (r = 2)		Direct (r = 1/2)		ΔE (eV)	Refs
	E_{indir} (eV)	B (cm.eV)$^{-1/2}$	E_{dir} (eV)	B (cm^{-2}.eV)		
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)	ΔT (°C)	H	Refs
B3T5	313	435	1048	122	0.39	Present
B5T3	305	431	1042	126	0.41	Present
$50B_2O_3.10PbO.10Al_2O_3.10ZnO.20Li_2O$	423	592	773	169	0.40	[1]
$75TeO_2.10TiO_2.15WO_3$	370	436	-	66	0.18	[12]
$48B_2O_325Li_2O.25NaF.2Dy_2O_3$	400	513	-	113	0,28	[13]
$60P_2O_5.20PbO.20ZnO$	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 ΔT 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 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 ΔT 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 ΔT and H give a large working range during operations for fiber drawing [1, 14].

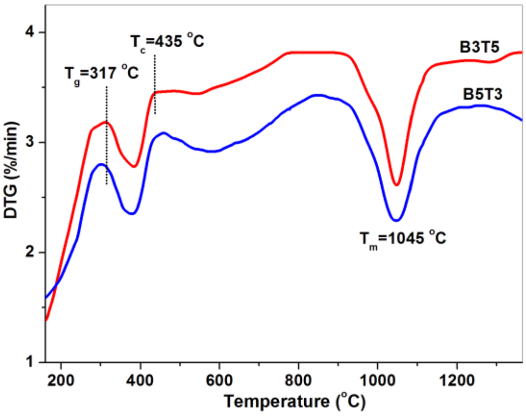

Fig. 5. DTA curve of borotellurite glass.

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] distorsed 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

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