

STRUCTURE AND PROPERTIES OF TeO₂- CONTAINING BORATE GLASSES

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Abstract

The structure and properties of TeO₂-containing B₂O₃-Al₂O₃-ZnO glasses were investigated. The glass transition temperature (T_g) decreases monotonically with an increase in the amount of TeO₂. The density also increases linearly with an increasing amount of TeO₂. XANES spectra indicate that TeO₄ trigonal bipyramids structural units are present uniformly in these glasses and this structural unit shares corners with BO₃ and BO₄ structural units. This reveals that TeO₂ is incorporated into borate structure as a glass former.

Keywords: TeO₂, borate glass, thermal properties, molar volume, XANES, trigonal bipyramids

Introduction

Tellurite glasses (high TeO₂-containing glasses) have received much attention as promising candidates for new glass because of their special properties (Yamada *et al.*, 1998; Murugan *et al.*, 2004, 2005; Zambelli *et al.*, 2004), high nonlinear refractive indices (Li *et al.*, 1998), large nonlinear optical sensitivity (Li *et al.*, 1998; Narazaki *et al.*, 1999; Tanaka *et al.*, 2000; Prakash *et al.*, 2001), relatively low phonon energy in the blue (Lee *et al.*, 1991) and green band emission (Kishino *et al.*, 2000), wide transmission window and good stability and durability (Ohishi *et al.*, 1998; Mori *et al.*, 2002; Murugan *et al.*, 2004, 2005). In addition, these glasses are well known to be good hosts for some rare earth and heavy metal ions with small multi-phonon decay rate (Gapontsev *et al.*, 1982; Wang *et al.*, 1994; Li

et al., 1998) and they are potential materials for up-conversion lasers (Xu *et al.*, 2005; Tamaoka *et al.*, 2006), optical filter amplifiers (Vetrone *et al.*, 2002), such as tellurite-base Er-doped fiber amplifier (Ohishi *et al.*, 1998), and non-linear optical devices, such as optical switching, optical memories, etc. (Li *et al.*, 1998).

However, high TeO₂-containing glasses often show the coloration, pale green to brilliant purple, depending on glass compositions and melting conditions (Konishi *et al.*, 2003; Khonthon *et al.*, 2008; Punpai *et al.*, 2008). This indicates that TeO₂ is readily reduced to low valence state species, such as Te₂, Te₂⁻, (Te)_n, etc. according to redox equilibrium. On the contrary, glasses exhibit colorless to pale yellow melted at low temperature and higher alkali

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concentration (Khonthon *et al.*, 2008).

In this study, properties and structure of TeO₂-containing borate glasses were investigated.

Experiment

Sample Preparation

TeO₂-containing borate glasses of (100 - X)[80B₂O₃ · 10Al₂O₃ · 10ZnO] · XTeO₂ (X = 0-30) were prepared by conventional melt-quench method. High purity alumina and reagent grade chemicals of H₃BO₃, ZnO, TeO₂ were used as raw materials. Batches corresponding to 30 g of glass were mixed thoroughly and melted in 50 cc alumina crucible at 1,000° - 1,200° C for 30 min depending on the glass composition in an electric furnace in air. After melting they were poured on to iron plate and pressed by another one. Then they were annealed at 400° - 500° C for 30 min depending on the glass composition in the furnace, and cooled slowly to room temperature in the furnace.

All glasses were pulverized to pass #200 sieve for DTA and X-ray absorption measurement. Hereafter, these glasses are referred to as Te-0, Te-10, Te-20, Te-30, respectively.

Density

The density of glasses was measured by Archimedes method using H₂O as a liquid at room temperature (30° C).

DTA

In order to determine the glass transition temperature (T_g), the differential thermal analysis (DTA) was carried out routinely using Perkin Elmer DTA-7 at the heating rate of 10° C/min.

X-ray Absorption Spectra

Te L_{III} (4,341 eV) edge X-ray absorption near edge structure (XANES) spectra were obtained on BL-8 beam line at Siam Photon Laboratory (NSRC, Thailand). The primary beam was obtained by a double crystal Si(111) monochromator. The energy steps and scan time were 0.2 eV/step and 5 times, respectively. The FL mode was applied. The reagent grade

chemical of α-TeO₂ (para-tellurite) was used as a standard.

Results and Discussion

Properties of Glasses

The properties of glasses are summarized in Table 1. Though Te-0 glass exhibits slight opaque because of phase separation, other glasses show pale yellow to pale brown.

Figure 1 shows the composition dependence of glass transition temperature. The glass transition temperature decreases linearly and rapidly with an increase in X at first and then decreases gradually. The glass transition temperature of pure TeO₂ glass was estimated by using data of Charton *et al.*, 2004.

Figure 2 shows the density of glasses as a function of glass composition. The density increases linearly with an increase in X. The density crystalline α-TeO₂ (para-tellurite) are also shown in these figures. By extrapolation of density to 100% of TeO₂ (para-tellurite crystal), a good linearity can be obtained.

TeO₂ can not be formed as a glass by itself and is not pure glass forming oxides unlike SiO₂, B₂O₃, etc. However, the addition of a very slight amount of second oxides leads to be formed as a glass. Thus, TeO₂ can be regarded as pseudo glass forming oxide. On the contrary, borate glasses often show boric oxide anomaly, which shows the minimum or maximum in relation between properties and composition by adding modifier oxides. In these glasses, no abnormal change in properties was observed, and hence TeO₂ is incorporated into B₂O₃ network structure gradually.

X-ray Absorption Spectra

Figure 3 shows the XANES spectra of Te-containing glasses. The pre peak was observed at around 4,345.5 eV for all glasses and TeO₂ standard (para-tellurite). The peak position does not change, but the peak intensity changes. The XANES spectra show that the valence state of Te ions was basically 4 in all glasses. For crystalline para-tellurite, this pre-peak looks like shoulder, however, this pre-peak becomes

Table 1. Properties of TeO₂- containing borate glasses

Glass	Appearance	Glass transition temperature T _g /°C	Density g/cm ³	Molar volume cm ³ /Mol
Te-0	Slightly opaque*	512	2.154	34.44
Te-10	Pale yellow	452	2.445	33.78
Te-20	Pale brown	396	2.817	32.37
Te-30	Pale brown	366	3.172	31.44
α-TeO ₂ (Standard)	Pale yellow (para-tellurite)	≈ 300**	5.660	28.20

* : Slightly phase separation,

** : 98TeO₂ · 2Ga₂O₃ glass (Charton and Armand, 2004)

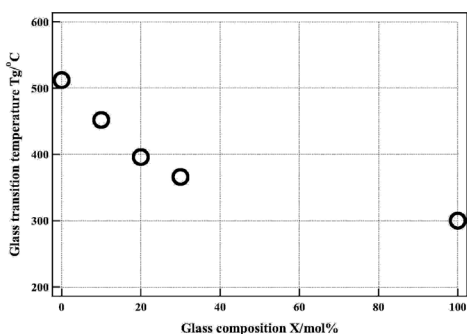


Figure 1. Glass transition temperature as a function of glass composition

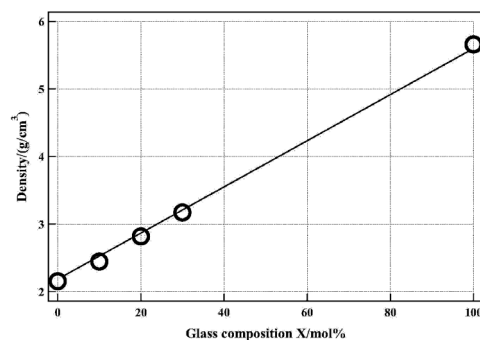


Figure 2. Density of glasses as a function of glass composition

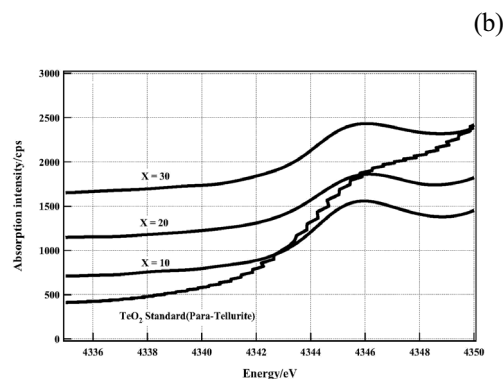
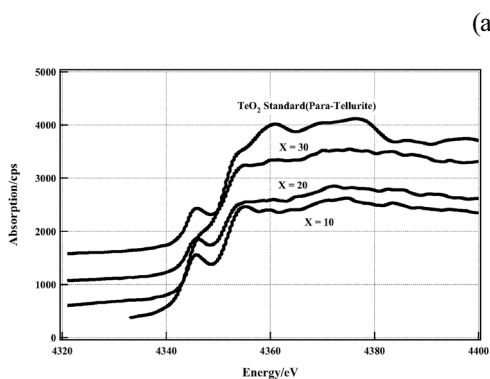


Figure 3. Te L_{III} edge XANES spectra of TeO₂- containing borate glasses
(a) Glasses with the references TeO₂ standard (para-tellurite).
(b) Zoom of the pre-edge

to be more clear and distinct in all glasses.

In crystalline α -TeO₂ (para-tellurite), TeO₄ trigonal bipyramidal structural unit shares their corners and forms three dimensional structure (Wells, 1975). This trigonal bipyramids structural unit is converted to trigonal pyramids by the addition of modifier oxides (Sabadel *et al.*, 1999; Charton *et al.*, 2002, 2004). Thus, the pre-peak in XANES spectra becomes to be more clear and distinct (Sabadel *et al.*, 1999; Charton *et al.*, 2002, 2004).

However, in B₂O₃-Al₂O₃-ZnO-TeO₂ glasses, the amount of modifier oxide is only 10 mol% and Al₂O₃ are present. Therefore, the amount of non-bridging oxygen ions must be the minimum, and TeO₂ incorporated might not form a trigonal pyramid. TeO₄ trigonal bipyramids structural unit disperses uniformly in B₂O₃ structural network and forms isolated TeO₄, and they share corners with BO₃ or BO₄ structural units. It seems that the intensity of pre-peak might increase.

Conclusions

The structure and properties of TeO₂-containing B₂O₃-Al₂O₃-ZnO glasses were investigated. The glass transition temperature (T_g) decreases monotonically with an increase in the amount of TeO₂. The density also increases and decreases linearly with an increasing amount of TeO₂.

XANES spectra indicate that TeO₄ trigonal bipyramids structural units are present uniformly in these glasses and this structural unit shares corners with BO₃ and BO₄ structural units. This reveals that TeO₂ is incorporated into borate structure as a glass former.

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