

THERMAL STABILITY AND PHYSICAL PROPERTIES OF PbO-B₂O₃-TeO₂ GLASS SYSTEM

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ABSTRACT

The effect of composition on the thermal stability and structural of the PbO-B₂O₃-TeO₂ glass has been studied. Homogeneous ternary (TeO₂)_y [(PbO)_x (B₂O₃)_{1-x}]_{1-y} glass system ($x = 0.0 - 0.50$ and $y = 0.7$) was prepared using a conventional melt-quenching method. The density, the molar volume, XRD, and the glass transition temperatures of prepared samples have been found to be compositional dependent. The increase of density and decrease of molar volume narrate with the high dense of PbO which relate to the constitution of the glass rather than the type of structural unit. The XRD result shows the partially crystalline precipitation and fit the partially crystalline state as the amount of PbO increases. From isothermal measurement, a criterion of Hruby's value (K_H) has been used to evaluate glass stability. Ultimately, it is observed that the thermal stability of lead-boro tellurite glass can be improved by increasing PbO in the glass composition. Nevertheless, the increasing amount of PbO also indicates the escalating of glass system rigidity. Raman spectrum indicates decreasing of O-Te-O and B-O-B bending shoulder at approximately 450 cm⁻¹ which ascribes the splitting of O-Te-O and B-O-B bonds and hence, the bridging oxygen's (BOs) were converted into NBOs.

Keywords: Raman spectra; Hruby's value; partially crystalline glass

INTRODUCTION

Tellurite glasses are very promising materials for laser and nonlinear application in optics due to some of their important characteristic features such as high refractive index, low phonon maxima and low melting temperature [1]. Furthermore, TeO₂ known as a conditional glass former, needs a modifier in order to easily form the glassy state.

The formation of glass on two glass formers is of both scientific and practical interest; where the structural network will be perturbed and may lead to the formation of new structural units [2]. Glass forming substances fall into two categories of either inorganic

compounds containing bonds which are partially ionic and partially covalent, or, inorganic or organic compounds which form chain structures with covalent bonds within the chains and van der Waals' bonds between the chains. Amorphous materials such as glasses are widely used in applications from medicine to transport to space flight. Glasses containing heavy metal oxide (HMO) have recently attracted the attention of several researchers for the excellent infrared transmission compared with conventional glasses. The structural and physical properties of PbO glasses are well described by Worrel and Henshell [3]. In a previous work [4], researchers have studied borate glasses containing heavy-metal oxides and shown that it has potential applications in radiation shielding.

The objective of the present work is to study the effect of PbO addition on the temperature stability, density and the crystalline phase of the lead boro-tellurite glass system besides serving as a significant guiding reference to those considering further research on physical properties of the material.

EXPERIMENTAL DETAILS

The ternary $(\text{TeO}_2)_y [(\text{PbO})_x (\text{B}_2\text{O}_3)_{1-x}]_{1-y}$ glass system likewise in Figure 1 ($x = 0.0$ - 0.50 and $y = 0.7$) were prepared using a conventional melt-quenching method. All the glass samples produced were homogenous, transparent and bubble free. The glasses were prepared by mixing together specific weights of tellurium dioxide - TeO_2 (Alfa Aesar 99.99%), lead oxide, litharge - PbO (99%) and boron oxide - B_2O_3 (Alfa Aesar, 97.5%). Appropriate amounts of TeO_2 , PbO and B_2O_3 were weighed by using an electronic balance having an accuracy of 0.0001 g. The chemicals were then thoroughly mixed in an agate pestle mortar for half an hour and poured into an alumina crucible. The crucible was then transferred to a furnace and heated at 950 °C for 60 minutes. The melt was then poured in a stainless steel cylindrical shaped split mould which had been preheated. The produced glass samples were then annealed at the temperature range 320- 350 °C depending on the composition for 2 hours. The prepared samples were then cut into several disc shapes for XRD and density measurements using Buhler ISOMET diamond cutter.

The density was measured at ambient temperature by Archimedes method, involving weighing in air and distilled water as the buoyancy liquid. All measurements were repeated 5 times and the average density were recorded. The accuracy of the results in duplicate measurements is 0.001 g/cm³. The molar volume was obtained through calculation.

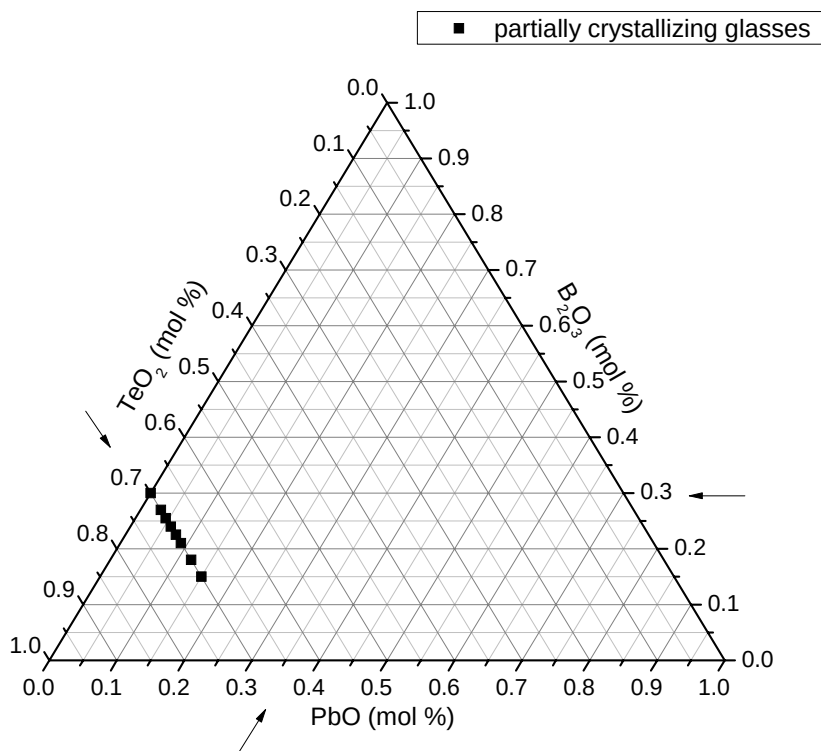


Figure 1: Glass composition under studies of $(\text{TeO}_2)_y [(\text{PbO})_x (\text{B}_2\text{O}_3)_{1-x}]_{1-y}$ system

Some of the samples were crushed into powder using an agate pestle mortar for DTA measurement. The equipment used was a SETARAM apparatus; the operating condition was; heating rate 2 K min^{-1} and DTA sensitivity $30 \mu\text{V mW}^{-1}$. The weight of all the specimens was approximately 20 mg.

The nature of glasses prepared was determined by X-ray diffraction examination using an X-ray diffractometer (Philips X'pert Pro Panalytical) using $\text{Cu-K}\alpha$ With a scan speed of 5° min^{-1} . The X-ray diffraction patterns were matched to JCPDS data and corresponding phases were identified. Eventually the samples were prepared in bulk form.

IR and Raman spectroscopy are similar in that both techniques provide information on vibrational frequencies. Raman spectra were measured using a Raman spectrometer (RSI 2001 B, Raman system, INC) equipped with a 532 nm solid-state diode green laser. Grams/32, version 6 software was used to analyse the spectra. All spectra were corrected for base line; smoothed and Fourier Transformed (FT). The baseline correction utilised the multiple point level method in which the baseline is levelled at a value that is the average of the baseline points. A constant correction factor of 80% of the degree of smoothing parameter was used throughout the data collection. The Fourier smoothing was accomplished by the peak data, applying a triangular filter function at the specified cut-off point of 40% and then reverse Fourier transforming the data.

RESULTS AND DISCUSSION

The density is affected by the structural softening/compactness, change in geometrical configuration, coordination number, cross-link density and dimension of interstitial spaces of the glass. Figure 2 shows the variation of density and molar volume with composition of ternary $(\text{TeO}_2)_y [(\text{PbO})_x (\text{B}_2\text{O}_3)_{1-x}]_{1-y}$ glasses. It is noted that, the density increases congruent with a decrease in the molar volume as the intermediate content increases. The increase in the density is related to the high dense PbO (9350 kg/m^3) compared to that of TeO_2 (5670 kg/m^3). This change in density by the addition of PbO is also related to the change in the atomic mass and atomic volume of constituent elements. The atomic mass of the Te, B and Pb atoms is 127.6, 10.81 and 207.19 and their atomic radii are 1.6, 0.98 and 1.75, respectively. It is clear that by increasing PbO , the molar volume decreases, which is the opposite to the variation of density with increasing PbO content. The increase in the density is related to the constitution of the glass rather than to the type of the structural unit, as observed earlier [5].

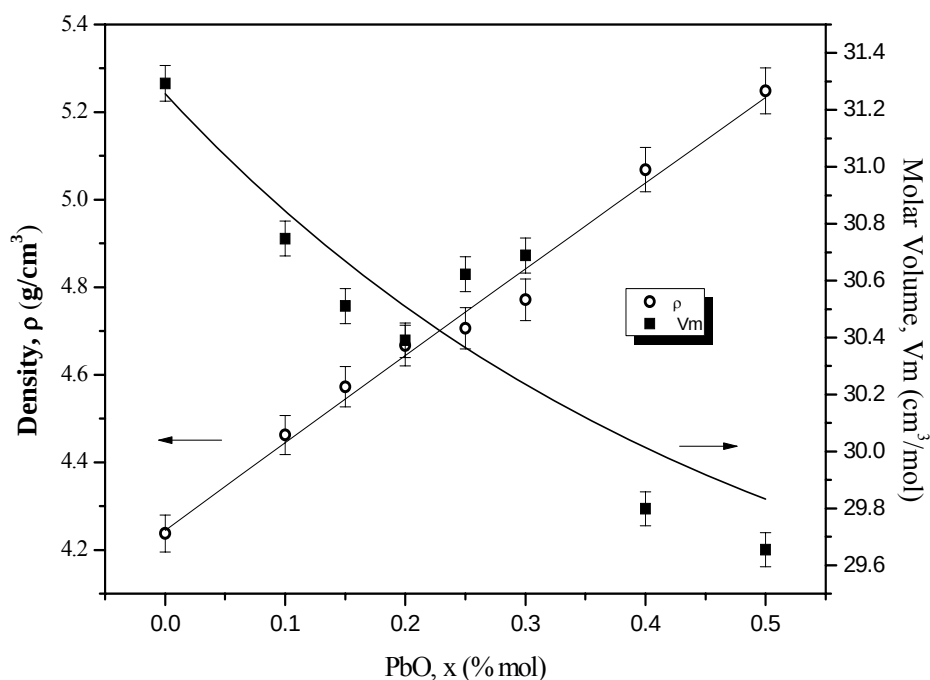


Figure 2: Variation of density and molar volume with composition of $(\text{TeO}_2)_y [(\text{PbO})_x (\text{B}_2\text{O}_3)_{1-x}]_{1-y}$

Figure 3 shows the DTA charts obtained for variation of density with composition of ternary $(\text{TeO}_2)_y [(\text{PbO})_x (\text{B}_2\text{O}_3)_{1-x}]_{1-y}$ glasses. The change in T_g in Table 1 indicates a change related to the manner in which PbO gets arranged in the glass. Eventually, the decrease in the glass transition temperature implies a decrease in the rigidity of the network [3]. The decrease of glass rigidity is due to addition amount of network

intermediate PbO. Eventually, addition of PbO - heavy metal oxide (HMO) - as an network intermediate into the binary borotellurite glasses results in splitting of O-Te-O and B-O-B bonds and hence, the bridging oxygen's (BOs) are converted into NBOs [6]. As a result, further addition of HMO into glass interstices, more ions being open up in the network. Thus, weakening of the glass structure or reduction in the rigidity of the network takes place.

In order to develop and use TeO₂ based glasses as non-linear optical materials or matrix glasses for heavy metal elements, an understanding of the thermal stability of glasses is necessary. Studies of the thermal stability and crystallization behaviour in TeO₂ based glasses, however, have been limited to a few papers to the author's knowledge. A criterion of Hruby's value (K_H) has been frequently used to evaluate glass stability [7]. According to this Hruby's equation, the larger K_H , the stronger is the inhibition to nucleation and crystallization processes, and consequently, the larger the thermal stability of the glass. Table 1 indicating that the thermal stability against crystallization is considerably high and increasing with the addition of PbO. This improved thermal stability is desirable in order to obtain a wide working-temperature range.

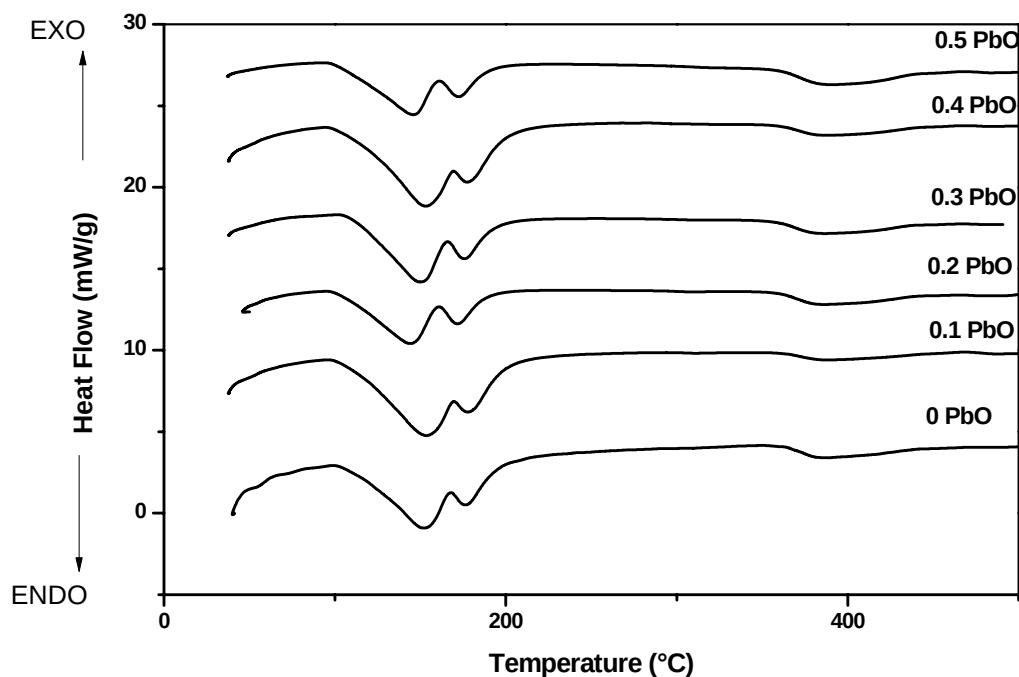


Figure 3: DTA curves of ternary (TeO₂)_y [(PbO)_x (B₂O₃)_{1-x}]_{1-y} glasses with varied compositions

Table 1: Thermal properties of $(\text{TeO}_2)_y [(\text{PbO})_x (\text{B}_2\text{O}_3)_{1-x}]_{1-y}$ glasses with varied compositions, T_g = (glass transition temperature), T_c = (an exothermic peak due to the crystal growth), T_m = (an endothermic effect due to the melting), K_H = (Hruby's thermal stability parameter $((T_c - T_g)/(T_m - T_c))$).

$[\text{TeO}_2]_{0.7}[(\text{B}_2\text{O}_3)_{1-x}(\text{PbO})_x]_{0.3}$	T_g (°C)	T_c (°C)	T_m (°C)	$(T_c - T_g)/(T_m - T_c)$
0	136.8	150	170.6	0.6408
0.1	135.9	152.7	173.6	0.8038
0.2	134.8	155.5	172.5	1.2176
0.3	131.2	157.3	170.2	2.0233
0.4	129.7	165.2	176.5	3.1416
0.5	128.7	165.7	178.1	2.9839

The XRD pattern in Figure 4 show the partially crystalline precipitation. Furthermore, the partially crystalline glass fit the amorphous state as the amount of PbO increases. It also shows the presence of a hunch for 2θ around $20^\circ - 35^\circ$. All these XRD reflections were assigned to the two polymorphic phases; hexagonal of tellurium and monoclinic of lead tellurate. The intensity of the XRD reflections indicate that more monoclinic crystals are reduced in quenched samples as the intermediate content increases. The structures of lead tellurate contain Pb_3TeO_6 probably consisting of TeO_3 trigonal pyramid connected by $3(\text{PbO})$ tetragonal forming a three-dimensional network.

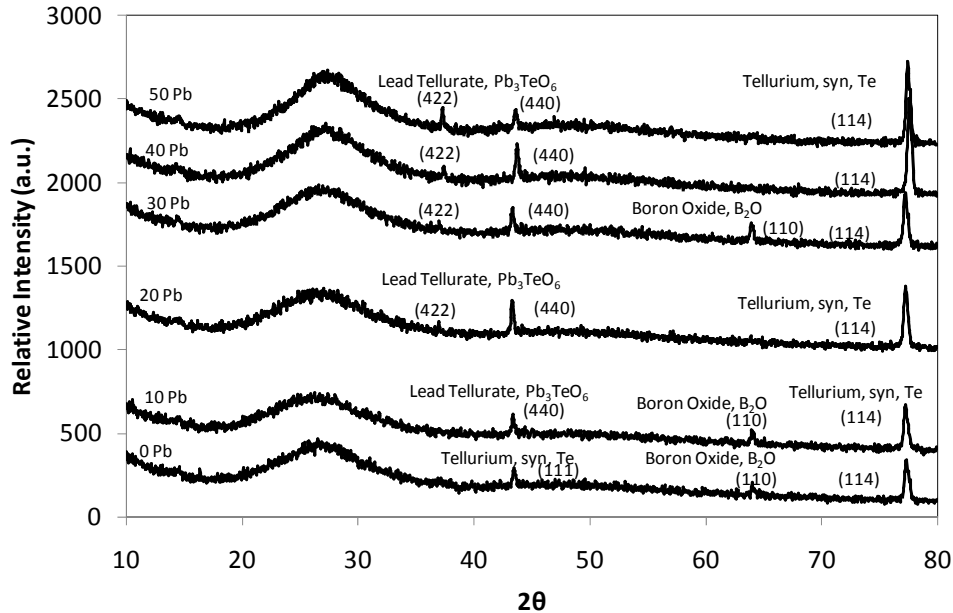


Figure 4: XRD patterns (at ambient temperature) of $(\text{TeO}_2)_y [(\text{PbO})_x (\text{B}_2\text{O}_3)_{1-x}]_{1-y}$ glasses with different compositions

Raman spectra in Figure 5 show increasing peak at $<100\text{cm}^{-1}$ which indicates the strong presence of Pb in the chemical bonding through vibrational mode due to addition of PbO. Decreasing on (symmetry stretching) Te-O-Te and B-O-B bending shoulder at approximately 490 cm^{-1} and 450 cm^{-1} ascribe that the splitting of Te-O-Te and B-O-B bonds and hence, the bridging oxygen's (BOs) are converted into NBOs. The spectral features from 710 cm^{-1} to 730 cm^{-1} and 790 cm^{-1} correspond to the TeO_4 bi-pyramidal arrangement and the TeO_{3+1} (or distorted TeO_4) and TeO_3 trigonal pyramids structures respectively. It can be clearly observed that the evolution of TeO_{3+1} and TeO_3 units occurs as the TeO_2 concentration decreases. Legitimately, the increasing peak on the TeO_3 trigonal pyramids shows that modification of lattice and interstitial occurs in the system.

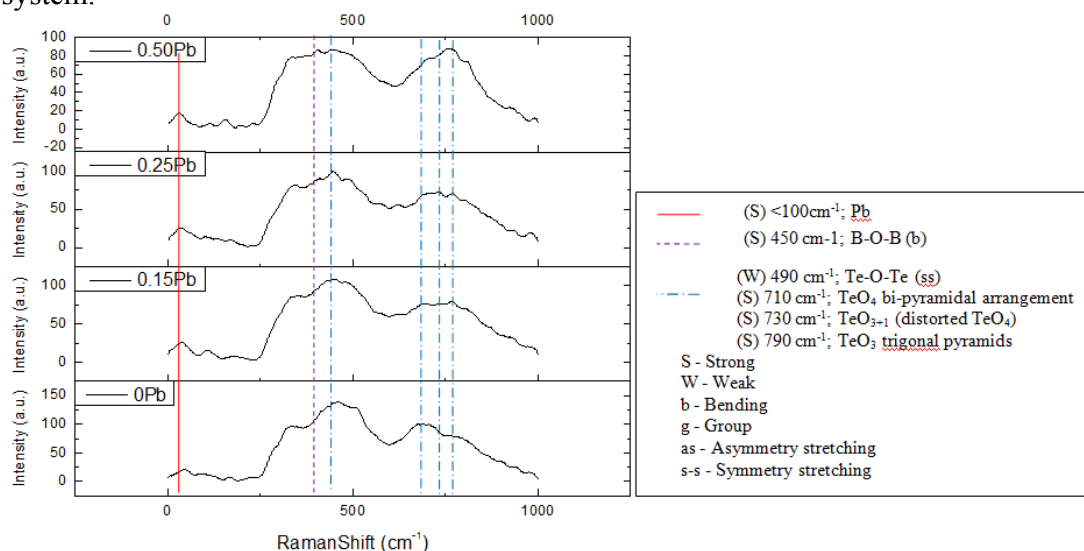


Figure 5: Raman spectra (at ambient temperature) of $(\text{TeO}_2)_y [(\text{PbO})_x (\text{B}_2\text{O}_3)_{1-x}]_{1-y}$ glasses with different compositions. In box is the marker labelling of Raman peak according to chemical bonding and stretching

CONCLUSION

Lead-boro tellurite glasses were successfully prepared. The structural rigidity and compactness of the glass were determined from the measurement of density and differential thermal analysis (DTA). The addition of PbO results leads to the increasing of density and molar volume. Furthermore, the accumulation results in splitting of O-Te-O and B-O-B bonds and hence, the bridging oxygen's (BOs) are converted into NBOs besides which leads to increase of rigidity in the glass network. The statement was supported by the glassy nature gained from the XRD measurement and Raman spectrum.

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REFERENCES

- [1] G. Vijaya Prakash, D. Narayana Rao and A.K. Bhatnagar, *J. Solid State Commun.*, **119** (2001) 39-44
- [2] M.A. Khaled, H. Elzahed, S.A. Fayek and M.M. El-Ocker, *Mater. Chem. Phys.*, **37** (1994) 329-332
- [3] A. Abd. El-Moneim, *Mater. Chem. Phys.*, **73** (2002) 318-322
- [4] Atul Khanna, S.S. Bhatti, K.J. Singh, K.S. Thind, *Nucl. Instr. and Meth. B* **114** (3-4) (1996) 217-220
- [5] Yasser B. Saddeek, *J. Alloys Comp.*, **467** (2009) 14–21
- [6] Yasser B. Saddeek, *Mater. Chem. Phys.*, **83** (2004) 222–228
- [7] Junjie Zhang, Jianbei Qiu, Yoji Kawamoto, *Mater. Lett.* **55**(2002) 77– 82