Thermal characteristics, Raman spectra, optical and structural properties of TiO_2-Bi_2O_3-B_2O_3-TeO_2 glasses

Nupur Gupta, Atul Khanna, Fernando Gonzàlez, and Reni Iordanova

Citation: AIP Conference Proceedings **1832**, 070005 (2017); doi: 10.1063/1.4980440
View online: http://dx.doi.org/10.1063/1.4980440
View Table of Contents: http://aip.scitation.org/toc/apc/1832/1
Published by the American Institute of Physics

Thermal Characteristics, Raman Spectra, Optical and Structural Properties of TiO_2-Bi_2O_3-B_2O_3-TeO_2 Glasses

Nupur Gupta[1], Atul Khanna[1*], Fernando Gonzàlez[2], Reni Iordanova[3]

[1]*Sensors and Glasses Physics Laboratory, Department of Physics, Guru Nanak Dev University, Amritsar-143005, Punjab, India*
[2]*Department of Chemistry and Process & Recourse Engineering, University of Cantabria, Santander-39005, Spain*
[3]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Blvd. 11, 1113 Sofia, Bulgaria*
**Email: atul.phy@gndu.ac.in*

Abstract. Tellurite and borotellurite glasses containing Bi_2O_3 and TiO_2 were prepared and structure-property correlations were carried out by density measurements, X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), Raman and UV-visible spectroscopy. Titanium tellurite glasses require high melt-cooling rates and were fabricated by splat quenching. On adding B_2O_3, the glass forming ability (GFA) enhances, and glasses could be synthesized at lower quenching rates. The density of glasses shows a direct correlation with molecular mass of the constituents. UV-visible studies were used to determine the optical band gap and refractive index. Raman studies found that the co-ordination number of tellurium ions with oxygen (N_{Te-O}) decreases with the increase in B_2O_3 as well as Bi_2O_3 content while, TiO_2 produce only a small decrease in N_{Te-O}, which explains the lower GFA of titanium tellurite glasses that do not contain Bi_2O_3 and B_2O_3. DSC studies show that the glass transition temperature (T_g) increases with B_2O_3 and TiO_2 concentrations and that T_g correlates well with bond enthalpy of the metal oxides.

Keywords: Tellurite and Borotellurite glasses, X-Ray Diffraction, Differential scanning calorimetry, Raman spectroscopy
PACS: 64.70.kj, 61.05.cp, 65.60.+a, 33.20.Fb.

INTRODUCTION

Tellurium oxide-based glasses have found remarkable technological applications due to their unique physical properties such as high refractive index, non-linear optical properties, high dielectric constant, wide optical transmission window [1]. The *ab-initio* studies show that the higher order of hyper-polarizability is inherent exclusively to the molecules having the form of linear chains formed from 'n' polymerized Te-O species [2].

The ternary TeO_2-based glassy systems containing TiO_2 modifier, jointly with Bi_2O_3 produces glasses which offer the best compromise on the high non-linear optical characteristics and the high mechanical and thermal resistance [3].

Bi_2O_3 is added to borotellurite glass to increase its density and to improve its structural and optical properties. The borotellurite glasses contain BO_4 tetrahedral, BO_3 trigonal units, TeO_4 trigonal bipyramidal, TeO_3 pyramidal and TeO_6 octahedral units at a high B_2O_3 content [4]. The aim of this work is to study the glass forming ability (GFA) of tellurite and borotellurite glasses containing Bi_2O_3 and TiO_2 and perform structure-property correlations by Differential Scanning Calorimetry (DSC), UV-Visible and Raman Spectroscopy.

EXPERIMENTAL

Tellurite and borotellurite glasses containing Bi_2O_3 and TiO_2 with composition: $xTiO_2$-yBi_2O_3-zB_2O_3-(100-x-y-z) TeO_2 (x=5, 10-mol%, y=5, 20 and 30-mol %, z=20 and 30-mol %) were prepared using TeO_2 (Aldrich 99%), Bi_2O_3 (Aldrich 99.9%), H_3BO_3 (Aldrich 99.9%), TiO_2 (Aldrich 99.9%) by melt-quench technique. Appropriate amounts of chemicals were weighed, and put in a platinum crucible after grinding and mixing chemicals. Sintering of the batch mixture was done at 250°C for 24 h in an electric furnace. The temperature of the furnace was then slowly raised to 900°C and the melt was kept at this temperature for 1 h, before quenching it on a heavy brass plate. Glasses without B_2O_3 were prepared by

DAE Solid State Physics Symposium 2016
AIP Conf. Proc. 1832, 070005-1–070005-3; doi: 10.1063/1.4980440
Published by AIP Publishing. 978-0-7354-1500-3/$30.00

splat quenching as these required higher cooling rates. The samples were characterized by density, XRD, DSC, UV-visible and Raman studies.

RESULTS AND DISCUSSIONS

XRD measurements were performed on Bruker D8 Focus X-ray Diffractometer using Cu K_α radiation in the 2θ range of 15° to 70°. Sharp peaks were absent in the XRD patterns but a broad hump in the range of 22° to 34° was present in all glasses, which confirmed the amorphous structure of all samples [Figure 1].

Density measurements were made by Archimedes method on an electronic balance. Density of samples increases from 5.67 g cm^{-3} in the sample: 5TiTe to 6.12 g cm^{-3} in the sample: 5Ti5BiTe, on incorporating Bi_2O_3 due to the high molecular weight of Bi_2O_3 (M.Wt = 465.96 amu) compared to that of TeO_2 (M.Wt = 159.6 amu). It is found that with the increase in the B_2O_3 concentration (M.Wt = 69.62 amu) and also TiO_2 (M.Wt = 79.90 amu) the density of glasses decreases as these lighter constituents replace the heavier TeO_2. Variation of density and molar volume along with DSC results are given in Table 1.

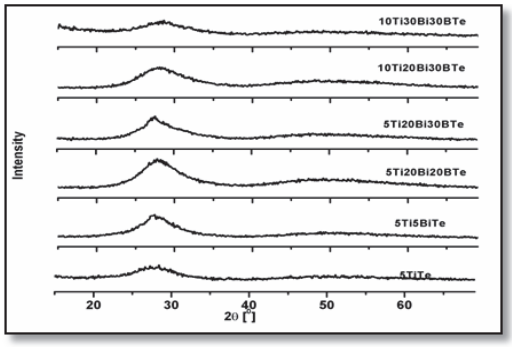

FIGURE 1. XRD patterns of glass samples.

DSC studies for the measurement of thermal properties such as glass transition temperature (T_g), crystallization temperature (T_c) and the liquidus temperature (T_m) was performed on SETARAM SETSYS Evolution-1750 system in the temperature range of 200-750°C at a heating rate of 10°C/min, in air flow of 20 ml/min. T_g increases significantly from 323°C to 394°C with increase in B_2O_3 content due to greater bond enthalpy of B-O bonds (804 kJ mol^{-1}) compared to that of Te-O bonds (376 kJ mol^{-1}). It was found that T_g increases with increase in the concentration of both TiO_2 and Bi_2O_3. The increase in T_g for both Bi_2O_3 (337.2 kJ mol^{-1}) and TiO_2 (666 kJ mol^{-1}) indicates that the Ti-O-Te and Bi-O-Te bonds are stronger than Te-O-Te linkages [3].

UV-visible studies for the measurement of optical absorption spectra of the polished disk shaped glass samples were performed on Shimadzu 1601 double beam UV-visible spectrophotometer in the wavelength range of 200-1100 nm. The absorption coefficient α(λ) was determined by dividing the absorbance A, with the thickness of glass samples and is shown in Figure 2.

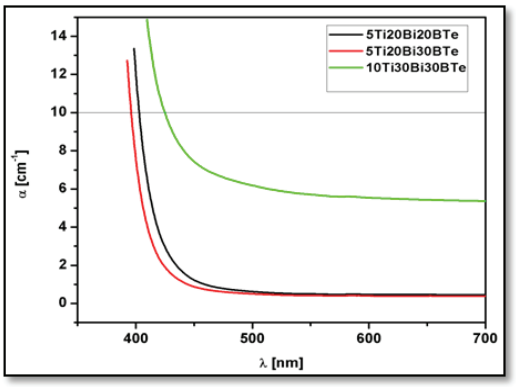

FIGURE 2. Optical absorption spectra of bismuth and titanium borotellurite glasses.

Optical band gap, E_g was calculated from the cut-off wavelength λ_o, which was arbitrarily defined as the wavelength at which α=10 cm^{-1}. λ_o shifts to lower wavelengths as the content of B_2O_3 is increased, while it shifts to larger wavelengths with increase in Bi_2O_3 mol% [Table 2].

E_g was used to calculate refractive index, η [3]. With increase in the Bi_2O_3 content, E_g decreases and η increases because Bi^{3+} ions have high polarity that leads to breaking of bridging oxygen to non-bridging oxygen (NBO). The increase in the band gap with increase in B_2O_3 content is due to the decrease in the

TABLE 1. Density, DSC and N_{Te-O} results of tellurite and borotellurite glasses containing Bi_2O_3 and TiO_2.

Sample Code	Composition (mol%)				Density(±0.01) (g cm^{-3})	T_g (°C)	N_{Te-O}
	TiO_2	Bi_2O_3	B_2O_3	TeO_2			
5TiTe	**5**	**-**	**-**	**95**	**5.67**	**323**	**3.65**
5Ti5BiTe	**5**	**5**	**-**	**90**	**6.12**	**328**	**3.50**
5Ti20Bi20BTe	**5**	**20**	**20**	**55**	**6.15**	**383**	**3.33**
5Ti20Bi30BTe	**5**	**20**	**30**	**45**	**5.93**	**394**	**3.31**
10Ti20Bi30BTe	**10**	**20**	**30**	**40**	**5.82**	**406**	**3.28**
10Ti30Bi30BTe	**10**	**30**	**30**	**30**	**6.39**	**410**	**3.22**

NBO concentration.

TABLE 2. Optical properties of tellurite and borotellurite glasses containing Bi_2O_3 and TiO_2.

Sample Code	λ_o[nm]	E_g[eV]	η
5Ti20Bi20BTe	403	3.08	2.37
5Ti20Bi30BTe	396	3.14	2.35
10Ti30Bi30BTe	425	2.92	2.42

Raman studies were performed on samples with Renishaw In-via Reflex micro-Raman spectrometer using 514.5 nm argon ion laser as excitation source, in the wavenumber range: 300 to 1000 cm^{-1}. Short-range structural properties of the glasses were elucidated from Raman studies. Raman spectra of glass samples are shown in Figure 3.

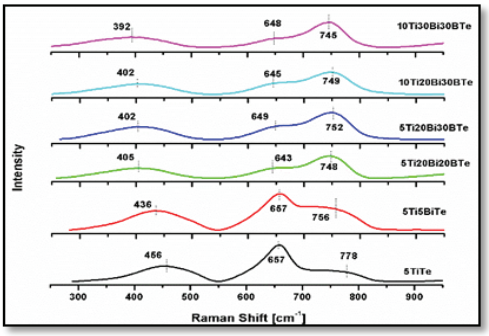

FIGURE 3. Raman spectra of tellurite and borotellurite glasses containing Bi_2O_3 and TiO_2.

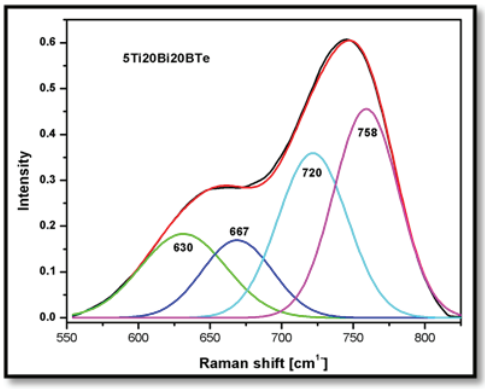

FIGURE 4. Deconvoluted Raman spectra of 5Ti20Bi20BTe glass sample.

Two characteristic Raman bands are observed in the wavenumber range: 400 to 500 cm^{-1} and 550 to 830 cm^{-1}. With the addition of modifier Bi_2O_3, the band in the range: 300 to 500 cm^{-1} shifts towards 300 cm^{-1} thus indicating that the stronger Te-O-Te and Te-O-Ti bridges are replaced by weaker Te-O-Bi linkages, relative to the spectrum of crystalline $Bi_2Te_4O_{11}$ [4]. The presence of Raman peak at 450 cm^{-1} is due to the stretching and bending vibrations of Te-O-Te linkages in TeO_4, TeO_{3+1} and TeO_3 structural units. The band at ~650 cm^{-1} is due to the Te-O stretching vibrations in TeO_4. The peak at 750–760 cm^{-1} becomes more prominent with the increasing content of Bi_2O_3 and is due to the stretching vibrations of Te-O bonds in TeO_3. This suggests that Bi_2O_3 causes an increase in TeO_3 at the expense of TeO_4 structural groups.

Raman spectra was de-convoluted and the peaks centered at ~630, 667, 720, 758 cm^{-1} were obtained, as shown in Figure 4 for one sample. The area under the peaks was used to calculate Te-O co-ordination using the formula [3]:

$$N_{Te-O} = 3 + \frac{A_{630}+A_{667}}{A_{630}+A_{667}+A_{720}+A_{758}} \qquad 1$$

The Te-O co-ordination number decreases from 3.50 to 3.22 on incorporating B_2O_3. This decrease in N_{Te-O} is due to the transformation of TeO_4 into TeO_3 structural units [3,4].

CONCLUSIONS

Tellurite and borotellurite glasses containing TiO_2 and Bi_2O_3 were fabricated and characterized by density, XRD, DSC, Raman and UV-visible studies. Density increases with increase in Bi_2O_3 due to its higher molecular weight. Glass transition temperature increases with both TiO_2 and Bi_2O_3, although Te-O co-ordination is not significantly modified by TiO_2. Glass forming ability of tellurite glasses containing TiO_2 and Bi_2O_3 enhances significantly on incorporating B_2O_3 into the tellurite network and is due to the structural transformation: $TeO_4 \rightarrow TeO_3$.

ACKNOWLEDGEMENT

Financial support from DST-Indo-Bulgarian project is acknowledged.

REFERENCES

1. R.A. El-Mallawany, *Tellurite Glasses Handbook: physical properties and data*. 2011: CRC Press.
2. M. Soulis, T. Merle-Méjean, A.P. Mirgorodsky, O. Masson, E. Orhan, P. Thomas and M.B. Smirnov, *Journal of Non-Crystalline Solids* **354**, 199-202 (2008).
3. N. Kaur and A. Khanna, *Journal of Non-Crystalline Solids* **404**, 116-123 (2014).
4. M. Udovic, P. Thomas, A. Mirgorodsky, O. Durand, M. Soulis, O. Masson, T. Merle-Méjean and J.C. Champarnaud-Mesjard, *Journal of Solid State Chemistry* **179**, 3252-3259 (2006).