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Citation: AIP Conference Proceedings **1832**, 070015 (2017); doi: 10.1063/1.4980450
View online: http://dx.doi.org/10.1063/1.4980450
View Table of Contents: http://aip.scitation.org/toc/apc/1832/1
Published by the American Institute of Physics

Short-Range Structure and Thermal Properties of Barium Tellurite Glasses

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Abstract. $BaO\text{-}TeO_2$ glasses containing 10 to 20 BaO mol% were prepared and characterized by X-ray diffraction, density measurements, differential scanning calorimetry and Raman spectroscopy. Glass density decreases with increase in BaO concentration from 10 to 20 mol%, due to replacement of heavier TeO_2 by lighter BaO, however glass transition temperature (T_g) increases significantly from a value of 318°C to 327°C due to increase in average single bond enthalpy of the tellurite network. Raman studies found that glass short-range structure consists of TeO_4 and TeO_3 structural units and BaO modifies the network by producing the structural transformation: $TeO_4 \rightarrow TeO_3$.

Keywords: Tellurite glasses, Thermal Properties, Raman studies.
PACS: 64.70.kj, 65.60.+a, 33.20.Fb.

INTRODUCTION

Tellurite glasses are considered as good candidates for efficient photonic, memory switching devices and gas sensing devices due to their a wide optical transmission windows, extraordinary nonlinear-optical properties, relatively low phonon energies, lack of toxicity, good durability and glass stability. The structural variability of tellurite glasses can be used to tailor the their thermal, optical and chemical durability parameters [1].This possibility has generated lot of interest in structural investigations of tellurite glasses. TeO_2 is a conditional glass former which requires very high quenching rates~10^5 to 10^6 K s^{-1} to form glass and modifiers such as metal oxides are added to enhance its glass forming ability and produce glasses at lower quenching rates of ~ 10^2 K s^{-1} [1, 2].The basic structural units of tellurite glasses are TeO_4 trigonal bipyramids (tbp) and TeO_3trigonal pyramid (tp). The addition of modifier BaO to the tellurite glasses breaks the random network and produces non-bridging oxygens (NBO) and substantial change in the glass network structure [3]. Barium tellurite glasses have ability to form a zero stress-optic and negative stress-optic response glasses [4]. Er^{3+}-doped barium tellurite glass with high upconversion and near-infrared (NIR) luminescence efficiency show great potential for infrared concentrator and NIR sensor and is also, a promising candidate for energetic mid IR lasers [5]. The present work is devoted to the synthesis and characterization of glasses from the system: $(BaO)_x(TeO_2)_{(100-x)}$.

EXPERIMENTAL

The binary $(BaO)_x(TeO_2)_{(100-x)}$ tellurite glasses with x=10,15,20 mol% were prepared. The Analytical Reagent grade chemicals of TeO_2 (Aldrich, India 99%) and $BaCO_3$ (CDH, India 99.9%) were used as starting materials. The chemicals were mixed and ground in an agate mortar pestle for about 30 min and then transferred to a platinum crucible. A homogeneous mixture of chemicals was melted in an electric furnace at 850°C for 20 min. Each glass sample was prepared by normal quenching in which the melt was poured on a brass block and a button shaped sample was prepared and immediately transferred to another furnace where it was annealed at 320°C for 30 min to avoid cracking by relieving internal stresses generated by quenching.

All samples were clear and transparent and characterized by X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and Raman Spectroscopy. The glassy state of samples was confirmed by XRD studies on Bruker D8 Focus X-ray diffractometer with Cu K_α radiation (λ=1.54056 Å) in

DAE Solid State Physics Symposium 2016
AIP Conf. Proc. 1832, 070015-1–070015-3; doi: 10.1063/1.4980450
Published by AIP Publishing. 978-0-7354-1500-3/$30.00

2θ range of 10°-70°. Density of glasses was measured by Archimedes method on an electronic balance of sensitivity 10^{-4} g using dibutylpthalate (DBP) as an immersion fluid. DSC studies were performed on a SETARAM SETYS 16 TG-DSC system in temperature range of 200–800°C at heating rate of 10°Cmin^{-1}. Raman studies were performed on Renishaw inVia Reflex Micro-Raman Spectrometer having 514.5 nm Argon Laser (50 mW), 2400 line/mm diffraction grating and an edge filter for recording the Stokes spectra and a Peltier cooled CCD detector.

RESULTS AND DISCUSSION

1.1 Structure

Figure 1 shows the XRD patterns of three barium tellurite glasses, all samples exhibit broad halos centered at 2θ ~27° and 50° due to the short-range order in the samples.

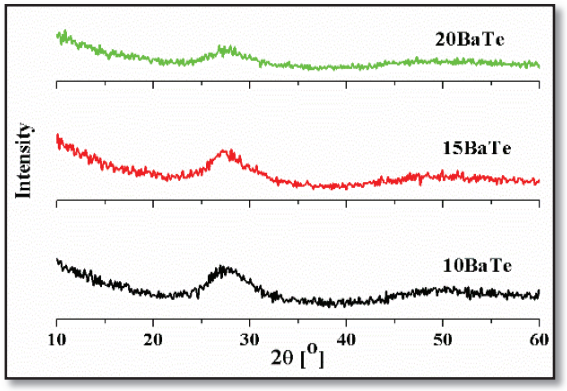

FIGURE 1. XRD patterns of BaO-TeO_2 glasses.

1.2 Density measurements:

It can be seen from Table 1 and Figure 2 that as the concentration of BaO increases from 10 to 20 mol%, density, d decreases from 5.58 to 5.52 g cm^{-3} while the molar volume, V_M increases slightly from 28.48 to 28.68 cm^{3}mol^{-1}.

the values are given in Table 1. Figure 3 shows that T_g increases with BaO molar concentration (glass modifier). Glass transition temperature characterizes the strength of the glass network. The parameter $\Delta T=T_c-T_g$ is commonly used to evaluate the glass stability against crystallization. The value of ΔT decreases from 143°C to 102°C on increasing BaO concentration. Hence, the thermal stability of glasses against devitrification decreases.

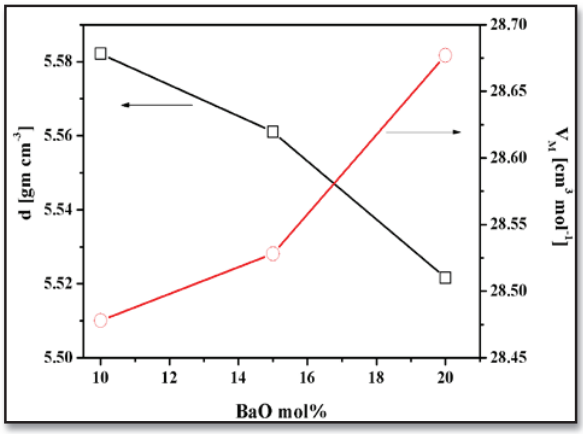

FIGURE 2. Variation of density and molar volume in BaO-TeO_2 glasses with BaO mol%.

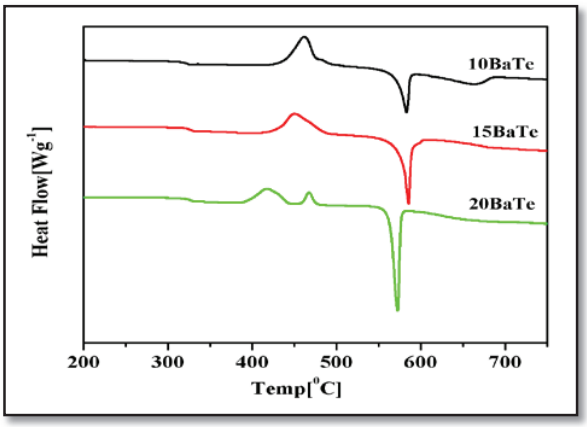

FIGURE 3. DSC patterns of BaO-TeO_2 glasses.

TABLE 1. Density, molar volume, N_{Te-O} and DSC data for barium tellurite glasses.

Sample Code	Composition mol.%		Density (d) (g cm^{-3})	Molar Volume (V_M) (cm^3 mol^{-1})	T_g (°C)	T_c (°C)		T_m (°C)		N_{Te-O}
	BaO	TeO_2				T_{c1}	T_{c2}	T_{m1}	T_{m2}	
10BaTe	10	90	5.58	28.48	318	461	-	582	662	3.54
15BaTe	15	85	5.56	28.53	325	450	-	585	-	3.42
20BaTe	20	80	5.52	28.68	327	435	488	600	-	3.43

1.3 DSC Results:

The thermal characteristics i.e. the glass transition temperature (T_g), crystallization temperature (T_c) and liquidus temperature (T_m) were measured by DSC and

1.4 Raman Study:

Figure 4 is the Raman spectra of three glasses which contains two broad bands in the ranges: 375-550 cm^{-1} (bending vibration of Te-O-Te linkages) and 550-840

cm^{-1} (stretching vibrations of TeO_4 tbp and TeO_3 tp structural units). The band at ~54 cm^{-1} is the boson peak, which is a universal feature of glassy phase. The Raman spectra were baseline corrected and deconvoluted with peaks centered at 609, 662, 719, 778 cm^{-1} (Figure 5). The co-ordination number of Te ions with oxygens was calculated from the area ratios of the deconvoluted bands [6]:

$$N_{Te-O} = 3 + \frac{A_{609}+A_{662}}{A_{719}+A_{778}+A_{609}+A_{662}} \qquad (1)$$

The Te-O coordination number decreases from a value of 3.54 to 3.43 with increase in BaO concentration from 10 to 20 mol%.

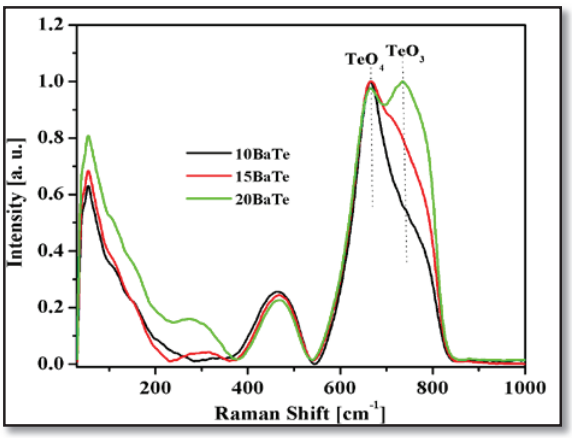

FIGURE 4. Raman spectra of $BaO\text{-}TeO_2$ glasses.

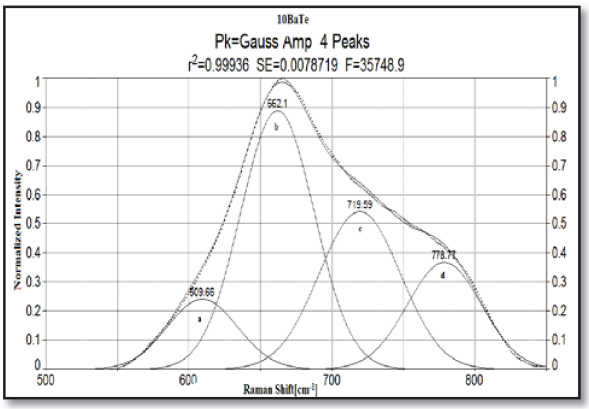

FIGURE 5. Deconvoluted Raman spectra of 10-mol.% BaO of Barium Tellurite glass.

CONCLUSIONS

Barium tellurite glasses were prepared and characterized by XRD, density, DSC and Raman studies. Glass density correlates directly with molecular mass of the constituents while T_g is a direct function of average single bond enthalpy of the network. Since the enthalpy of Ba-O bonds (562 kJ mol^{-1}) is significantly higher than that of Te-O bonds (376 kJ mol^{-1}), Tg increases with BaO concentration. The Raman spectra of the glasses were interpreted in terms of the structural transformations produced by BaO. Increasing content of BaO accelerates the conversion of TeO_4 and TeO_{3+1} into TeO_3 units having non-bridging oxygens.

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