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Short-Range Structure and Thermal Properties of Lead Tellurite Glasses

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Abstract. PbO-TeO_2 glasses having composition: xPbO–$(100-x)TeO_2$ (x = 10, 15 and 20 mol%) were prepared by melt quenching and characterized by X-ray diffraction, density measurements, differential scanning calorimetry and Raman spectroscopy. Glass density increases from 5.89 to 6.22 g cm^{-3} with increase in PbO concentration from 10 to 20 mol%, due to the replacement of TeO_2 by heavier PbO. DSC studies found that glass transition temperature (T_g) decreases from a value of 295°C to 281°C. Raman studies found that glass short-range structure consists of TeO_4 and TeO_3 structural units and that PbO modifies the network by the structural transformation: TeO_4 to TeO_3.

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

INTRODUCTION

Tellurium oxide glasses have generated great interest over the years as potential optoelectronic materials given their unique electronic structures and processing flexibility in the non-crystalline form [1]. Tellurite glasses are being increasingly explored as broadband fiber optic Raman amplifiers for use in nonlinear and ultrafast optics and optical telecommunications [2]. 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]. The basic structural units of tellurite glasses are TeO_4 trigonal bipyramids (tbp) and TeO_3 trigonal pyramid (tp). The addition of modifier PbO to the tellurite glasses breaks the random network and produces non-bridging oxygens (NBO) and substantial change in the glass network structure [3]. The present work is devoted to the synthesis and characterization of glasses from the system: $(PbO)_x(TeO_2)_{(100-x)}$.

EXPERIMENTAL

The binary $(PbO)_x(TeO_2)_{(100-x)}$ tellurite glasses with x=10,15 and 20 mol% were prepared. The analytical reagent grade chemicals of TeO_2 (Aldrich, India 99%) and PbO (Aldrich, 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 700°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 2θ range of 10°-52°. Density of glasses was measured by Archimedes method on an electronic balance of sensitivity 10^{-4} g using dibutyl pthalate (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°C min^{-1}. Raman studies were performed on

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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 lead tellurite glasses, all samples show broad halos centered at 2θ ~27° and no peaks were observed, therefore the samples were amorphous.

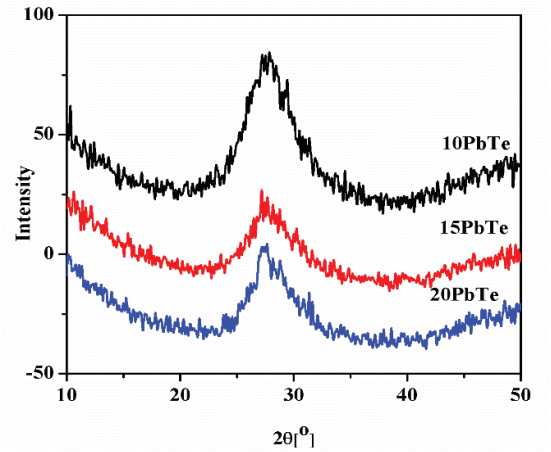

FIGURE 1. XRD patterns of PbO-TeO_2 glasses.

1.2 Density measurements:

It can be seen from Table 1 and Figure 2 that as the concentration of PbO increases from 10 to 20 mol%, density, d increases from 5.89 to 6.22 g cm^{-3} while the molar volume, V_M decreases slightly from 28.14 to 27.68 $cm^3 mol^{-1}$.

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 increases slightly from 47°C to 50°C on increasing PbO concentration. Hence, the thermal stability of glasses against devitrification is nearly constant.

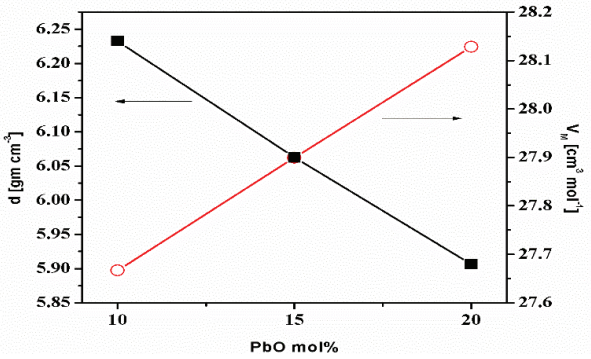

FIGURE 2. Variation of density and molar volume in PbO-TeO_2 glasses with PbO mol%.

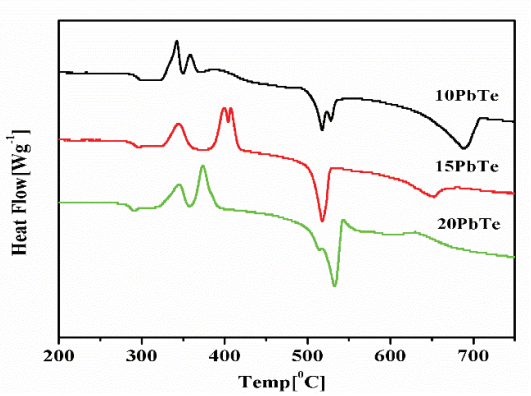

FIGURE 3. DSC patterns of PbO-TeO_2 glasses.

TABLE 1. Density, molar volume, N_{Te-O} and DSC data for lead 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}
	PbO	TeO_2				T_{c1}	T_{c2}	T_{m1}	T_{m2}	
10PbTe	10	90	5.89	28.14	295	342	358	517	528	3.47
15PbTe	15	85	6.06	27.90	291	343	400	517	652	3.42
20PbTe	20	80	6.22	27.68	281	334	373	531	-	3.38

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 the values are given in Table 1. Figure 3 shows that T_g decreases with PbO molar concentration (glass modifier). Glass transition temperature characterizes

1.4 Raman Study:

Figure 4 shows the Raman spectra of glasses which contains three broad bands, for glass with 10-mol% PbO it is 265-544 cm^{-1}, for 15-mol% sample it is 363-544 cm^{-1} and for 20-mol% PbO it is 370-544 cm^{-1} due to bond bending vibration of Te-O-Te linkages and a second band: 557-838 cm^{-1} due to stretching vibrations of TeO_4 tbp and TeO_3 tp structural units. The band at ~

52 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 599, 652, 701, 769 cm^{-1} (Figure 5). The co-ordination number of Te ions with oxygens was calculated from the intensity ratios of the deconvoluted bands [4]:

$$N_{Te-O} = 3 + \frac{I_{599} + I_{652}}{I_{599} + I_{652} + I_{701} + I_{769}} \quad (1)$$

Where I denotes the intensities of the Raman peaks. The Te-O coordination number decreases from a value of 3.47 to 3.38 with increase in PbO concentration from 10 to 20 mol%.

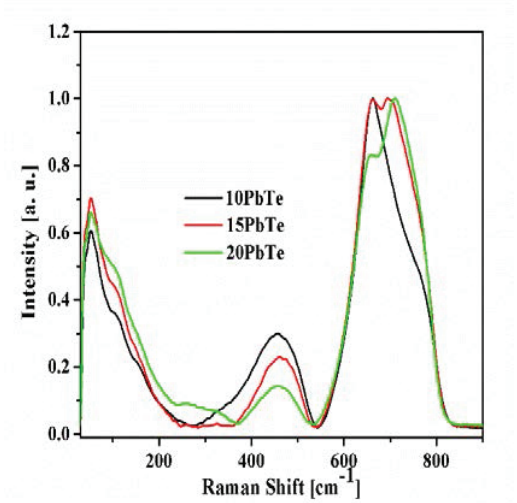

FIGURE 4. Raman spectra of PbO-TeO_2 glasses.

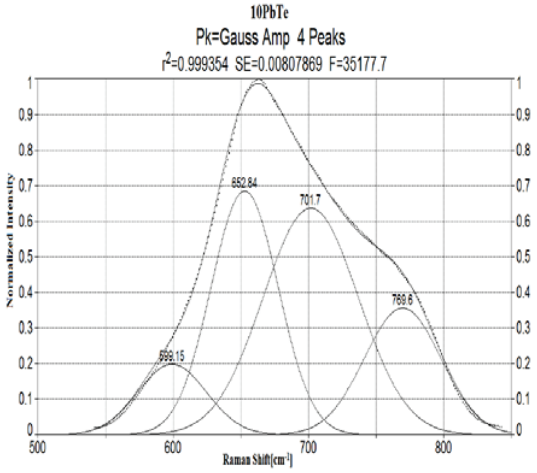

FIGURE 5. Deconvoluted Raman spectra of 10mol% lead tellurite glass.

CONCLUSIONS

Lead tellurite glasses were prepared by melt quenching and characterized by XRD, density, DSC and Raman studies. Glass density correlates directly with molecular mass of the constituents. Glass transition temperature decreases with PbO concentration. The Raman spectra of the glasses were interpreted in terms of the structural transformations produced by PbO. Increasing content of PbO accelerates the conversion of TeO_4 and TeO_{3+1} into TeO_3 units having non-bridging oxygens.

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