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DSC and Raman Studies of Silver Borotellurite Glasses

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Abstract. Silver borotellurite glasses of composition: xAg_2O-yB_2O_3-$(100\text{-}x\text{-}y)TeO_2$ (x=20-mol%, y = 0, 10, 20 and 30-mol%) were prepared and characterized by density, X-ray diffraction (XRD), differential scanning calorimetry, and Raman spectroscopy. XRD confirmed the amorphous structure of all samples. Density of glasses decreases while the glass transition temperature increases with increase in B_2O_3 content from 10 to 30-mol%. Raman study shows that coordination number of Te with oxygen decreases steadily from 3.42 to 3.18 on adding B_2O_3 due to the transformation of TeO_4 into TeO_3 units.

Keywords: Borotellurite glasses, X-ray Diffraction, Differential Scanning Calorimetry, Raman spectroscopy.
PACS: 64.70.kj, 61.05.cp, 65.60.+a, 33.20.Fb.

INTRODUCTION

Oxide glasses containing metal oxides have been studied for their interesting optical and electrical properties [1, 2]. Tellurite glasses have several useful properties like high refractive index, high glass forming ability, low melting points, good chemical durability, low phonon maxima and non-hygroscopic nature. These glasses have high non-linear refractive indices due to lone electron pair of Te^{4+} ions [3-6]. Tellurium oxide is a conditional glass former; pure tellurite glass can be formed at very high quenching rates of ~10^5 K/s, it has Te-O coordination number, $N_{Te\text{-}O}$ = 3.69 [7]. On incorporating metal oxides, Te-O coordination and glass properties get modified.

In tellurite glasses, the basic structural units are TeO_4 trigonal bipyramids (tbp) and TeO_3 trigonal pyramid (tp) [8]. The addition of metal oxides in tellurite glass causes breakage of Te-O-Te linkages, thereby resulting in systematic conversions of TeO_4 into TeO_3 structural units that contain doubly bonded terminal oxygens i.e. Te=O bonds [5, 7].

Silver oxide acts as a modifier in the tellurite glass network and enhances the electrical conductivity of tellurite glasses. B_2O_3 is the best glass former and its addition in silver tellurite glasses modifies the glass network through the conversion of TeO_4 into TeO_3 [9]. The aim of this work is to study the thermal properties and short-range structural properties of silver borotellurite glasses by Differential Scanning Calorimetry (DSC) and Raman spectroscopy.

EXPERIMENTAL

Silver borotellurite glasses having composition: xAg_2O-yB_2O_3-$(100\text{-}x\text{-}y)TeO_2$ (x =20-mol%, y =0, 10, 20 and 30-mol%) were prepared using TeO_2 (Aldrich 99%), $AgNO_3$ (Qualigens 99.8%) and H_3BO_3 (Aldrich 99.9%) by splat quenching technique. Appropriate amounts of chemicals were weighed, mixed together and put in a Pt crucible. The batch mixture was sintered at 250°C for 24h in an electric furnace. The furnace temperature was then slowly raised to 950°C and the melt was kept at this temperature for 30 min, subsequently a small quantity of the melt was poured and pressed between two heavy metal plates. Samples were characterized by density measurements, X-ray diffraction (XRD), DSC and Raman spectroscopy.

RESULTS AND DISCUSSION

XRD measurements were performed on Bruker D8 Focus X-ray diffractometer using Cu K_α radiation (λ=1.5406Å) in the 2θ range of 10 to 60°. XRD patterns do not show any sharp peaks, but broad hump from 25 to 30 degree which confirms the amorphous structure of all samples [Figure. 1].

Density of glasses was measured by Archimedes method using an electronic balance of sensitivity 10^{-4} g. Density of samples decreases from 6.282 to 5.101 g cm^{-3} as B_2O_3 content increases due to replacement heavier TeO_2 (159.6 amu) by lighter B_2O_3 (69.62 amu)

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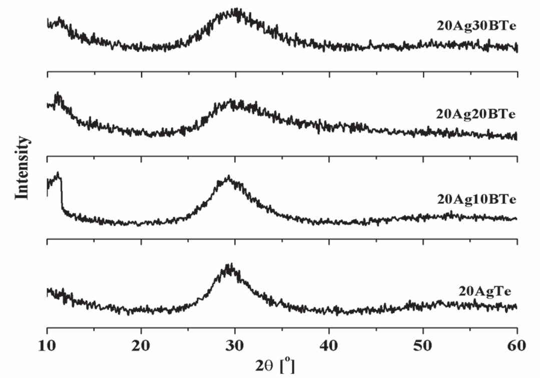

FIGURE 1. XRD patterns of Ag_2O-B_2O_3-TeO_2 glasses.

[Table 1]. Both density and molar volume decreases on adding B_2O_3 in silver tellurite glass. This anomalous behavior has also been reported in other glass systems [4, 10]. Variation of density and molar volume of Ag_2O-B_2O_3-TeO_2 glasses with B_2O_3 mol% is shown in Figure 2.

TABLE 1. Density, molar volume and DSC data for silver-borotellurite 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)
	Ag_2O	B_2O_3	TeO_2			T_{g1}	T_{g2}		
20AgTe	20	-	80	6.282	27.70	214	-	288	451
20Ag10BTe	20	10	70	5.973	27.63	240	-	349	438
20Ag20BTe	20	20	60	5.936	26.29	263	330	384	421
20Ag30BTe	20	30	50	5.101	28.83	289	461	-	-

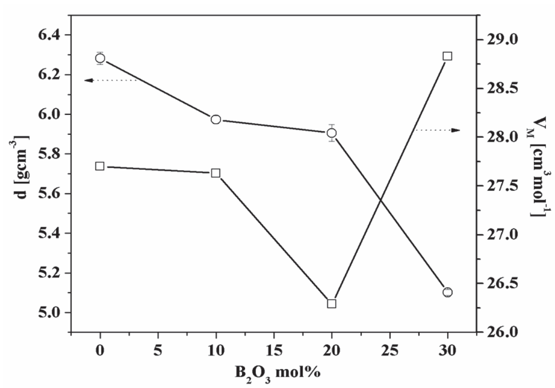

FIGURE 2. Variation of density and molar volume in Ag_2O-B_2O_3-TeO_2 glasses with B_2O_3 mol%.

Thermal properties such as glass transition temperature (midpoint value, T_g), crystallization (peak point, T_c) and liquidus temperatures (peak point, T_m) were measured by DSC. These studies were performed

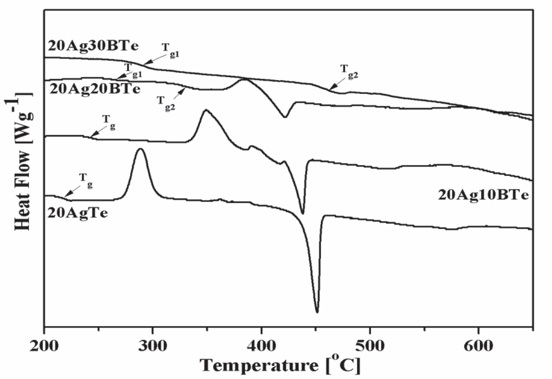

FIGURE 3. DSC patterns of Ag_2O-B_2O_3-TeO_2 glasses.

on SETARAM SETSYS Evolution-1750 system in the temperature range of 200-650°C at a heating rate of 10°C/min, in air flow of 20 ml/min.

DSC patterns of silver tellurite glasses are shown in Figure 3. It is found that T_g increases from 214 °C to 289°C with increase in B_2O_3 mol% due to the greater bond enthalpy of B-O (804 kJ mol^{-1}) than Te-O (376 kJ mol^{-1}) and due to the formation of metal ion-oxygen bonds with terminal oxygens that increases the strength of glass network [11, 12]. Glasses with 20 and 30-mol % show double glass transitions in DSC scans [Figure. 3], which indicates phase separation. Sample with 30-mol% B_2O_3 does not show crystallization and melting peaks. Glass transition temperature characterizes the strength of the glass network. Values of glass transition, crystallization and liquidus temperatures are given in Table 1.

Short-range structure of glasses was studied by Raman spectroscopy. Raman spectra of glasses were recorded at room temperature using Renishaw InVia Raman Microscope. The excitation wavelength was 514.5 nm. Figure 4 shows the Raman spectra of silver borotellurite glasses. Samples show two characteristic Raman bands in the wavenumber ranges: 400 to 530

cm^{-1} and 550 to 820 cm^{-1}. Strong peak at low wavenumbers of ~55 cm^{-1} is the boson peak and is characteristic feature of glasses [9]. The Raman band in range 400 to 530 cm^{-1} is due to bending vibration of Te-O-Te linkages, similarly the band in range of 550 to 810 cm^{-1} is assigned to stretching vibrations of TeO_4 tbp and stretching vibrations of TeO_3 tp structural units [5, 8]. The Raman spectra were deconvoluted with peaks centered at 461, 608, 656, 700 and 745 cm^{-1}. The areas under the peaks were used to determine the Te-O coordination number by using following formula [12]:

$$N_{Te-O} = 3 + \frac{A_{608} + A_{656}}{A_{608} + A_{656} + A_{700} + A_{745}}$$

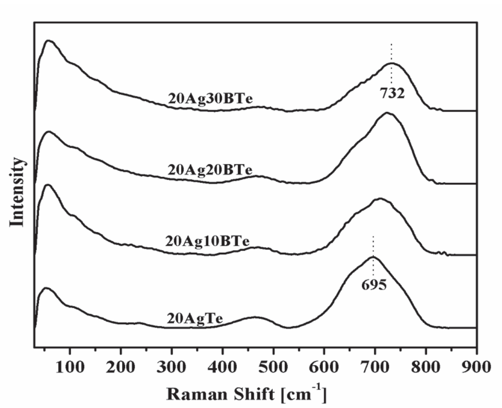

FIGURE 4. Raman spectra of Ag_2O-B_2O_3-TeO_2 glasses.

The peak at 695 cm^{-1} shifts to 732 cm^{-1} and N_{Te-O} decreases from 3.42 to 3.18 with increase in B_2O_3 concentration [Figures 4-5 & Table 2]. Decrease in N_{Te-O} is due to the transformation of TeO_4 into TeO_3 structural units on incorporating B_2O_3.

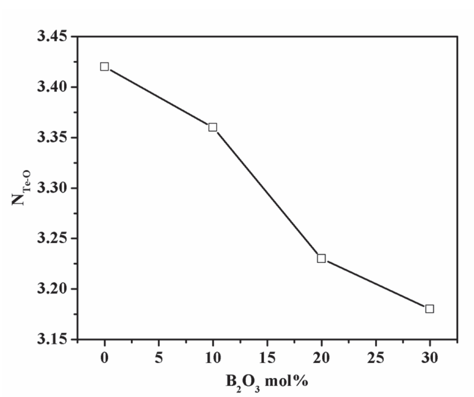

FIGURE 5. Variation of N_{Te-O} with B_2O_3 mol% in Ag_2O-B_2O_3-TeO_2 glasses.

TABLE 2. Te-O coordination number, N_{Te-O} in silver tellurite and borotellurite glasses.

Sample code	Raman peaks area ratio	N_{Te-O}
20AgTe	0.42	3.42
20Ag10BTe	0.36	3.36
20Ag20BTe	0.23	3.23
20Ag30BTe	0.18	3.18

CONCLUSIONS

Silver borotellurite glasses were prepared and characterized by density, XRD, DSC and Raman spectroscopy. Density of glasses decreases from 6.282 to 5.101 gcm^{-3} and glass transition temperature increases from 214°C to 289°C on adding B_2O_3 up to 30-mol%. Increase in T_g is due to the strengthening of glass network. Raman studies found N_{Te-O} decreases from 3.42 to 3.18 on adding 30-mol % of B_2O_3 in silver tellurite glasses due to increase in concentration of TeO_3 units.

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