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Structural and Thermal Properties of Vanadium Tellurite Glasses

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Abstract. V_2O_5 - TeO_2 glasses containing 10 to 50 mol% V_2O_5 were prepared by melt quenching and characterized by X-ray diffraction (XRD), density, Differential Scanning Calorimetry (DSC) and Raman studies. XRD confirmed the amorphous nature of vanadium tellurite samples. The density of the glasses decreases and the molar volume increases on increasing the concentration of V_2O_5 . The thermal properties, such as glass transition temperature T_g , crystallization temperature T_c , and the melting temperature T_m were measured. T_g decreases from a value of 288°C to 232°C. The changes in T_g were correlated with the number of bonds per unit volume, and the average stretching force constant. Raman spectra were used to elucidate the short-range structure of vanadium tellurite glasses.

INTRODUCTION

Tellurium dioxide (TeO_2) is the most stable oxide of tellurium (Te). The transitional position of Te between metals and non-metals, has long held special significance and the properties of tellurium oxide such as good glass stability and durability, low melting point, non-hygroscopic nature; high refractive indices, wide optical transmission window, and exceptional non-linear optical properties are the driving force behind the enormous interest in the synthesis and characterization of tellurite materials[1]. Due to aforementioned unique properties, the tellurite glasses have wide range of applications in gas sensors, memory switching devices, up-conversion laser and optical waveguides. In tellurite glasses, there are two types of structural units; TeO_4 trigonal bipyramids (tbp) and TeO_3 trigonal pyramids (tp). TeO_2 has two crystalline phases, namely α - TeO_2 (paratellurite) and β - TeO_2 (tellurite) with tetragonal and orthorhombic structures respectively. The structure of α - TeO_2 consists of a three-dimensional (3D) network built up from TeO_4 subunits, with each oxygen atom shared by two units, bonded in the equatorial position to one tellurium atom and in the axial position to another tellurium atom. On slowly heating the pure glass, γ - TeO_2 phase is formed which gets modified to α - TeO_2 with further thermal energy while the β - TeO_2 phase is not observed during this process[2]. Earlier, pure tellurite glasses were formed at very high quenching rates of $\sim 10^5 Ks^{-1}$ by twin roller quench technique but recently it has been synthesized in bulk using intermittent quenching technique[3]. The molecular dynamics simulation studies show the coordination number of Te-O to be 3.69, while by neutron diffraction studies, it is reported to be 3.73. The N_{Te-O} values calculated from neutron diffraction studies show good agreement with the results from Raman spectroscopy[2].

Tellurium dioxide is a conditional glass former and it forms glasses easily when mixed with metal oxides such as Li_2O , BeO , MgO , SrO , V_2O_5 etc. The addition of modifiers in tellurite glass causes the breakage of Te-O-Te linkages and to break one edge in TeO_2 , an oxygen atom must be supplied to complete the octets of the two cations involved. Therefore different oxides of groups III, IV, or V of the periodic table can be used to synthesize binary tellurite glasses. It is reported that with increase in proportion of modifiers, the network first breaks down to cross-linked and branched chains and finally to un-branched chains[4]. Generally, this deformation is related with the change in the coordination structure of the tellurium atoms. For instance, TeO_4 (trigonal bipyramids) converts into TeO_3 (trigonal pyramids) with the addition of the alkali oxides[5].

Pure, single crystal, vanadium penta-oxide (V_2O_5) is an insulator due to the presence of empty d-bands. After growing it from the melt, it is found to be an n-type semiconductor having activation energy of around 0.28eV. This

might happen because of the impurities arising from doping or due to the loss of oxygen from the melt[4]. V_2O_5 can act as a network former, and also as network modifier in the presence of TeO_2 since it produces structural modification in the tellurite network. On mixing it with TeO_2 , it forms glasses in the composition range of 7.5 to 58 mol% of V_2O_5 [1]. The glass transition temperature(T_g) depends on the concentration of V_2O_5 and it is observed that the glass structure gradually changes from the continuous tellurite network to the continuous vanadate network with increasing V_2O_5 content from 20 to 50 mol%, with large concentration of triangularly co-ordinated Te atoms. However, the glasses containing less than 20 mol% V_2O_5 have a continuous tellurite network that contains mostly four-coordinated Te atoms [6]. The aim of this work is to study the compositional dependence of T_g and short-range structural properties of vanadium tellurite glasses by DSC and Raman spectroscopy.

EXPERIMENTAL

Glass Preparation

Vanadium tellurite glasses of compositions: $xV_2O_5-(100-x)TeO_2$ where $x= 10, 30, 40, 50$ mol% were prepared using TeO_2 (Sigma Aldrich India 99%) and V_2O_5 (Sigma Aldrich India 99.6 %) by normal quenching. The appropriate amount of these starting materials were weighed and mixed together in an agate mortar-pestle. The mixture was put into a platinum crucible (25 cm^3). The batch mixture was first sintered at 250°C in electric furnace for 3h followed by second sintering at 450°C for 2h. The temperature of furnace was slowly raised to 700°C and the glass melt was kept at this temperature for 1h before quenching it on a heavy brass plate. The samples were immediately annealed at 230°C for 1h to reduce thermal stresses in the samples. The samples were characterized by density measurements, XRD, DSC and Raman studies.

X-ray diffraction (XRD)

XRD studies were carried out on Shimadzu XRD-7000 X-ray diffractometer with $Cu\ K_{\alpha 1}$ radiation ($\lambda = 1.54056\text{ \AA}$) in the 2θ range of $15^\circ - 70^\circ$. The X-ray tube was operated at 40 kV and 30 mA and the scattered X-ray intensity was measured with a scintillation detector.

Density measurement

Density of glasses was determined by Archimedes method using dibutylphthalate as the immersion fluid. The error in density was in the range of ± 0.01 to 0.04 g cm^{-3} .

Differential Scanning Calorimetry (DSC)

DSC studies were performed on powdered samples(20-50 mg)in platinum pans on SETARAM SETYS 16 TG-DSC system at heating rate of $10^\circ\text{C min}^{-1}$ under air-flow conditions in the temperature range of $200-800^\circ\text{C}$. The maximum uncertainty in the measurement of glass transition (mid-point), crystallization (peak-point) and melting temperatures (peak-point) is $\pm 1^\circ\text{C}$.

Raman spectroscopy

Raman studies were performed on powdered samples using Renishaw In-Via Reflex micro-Raman spectrometer with 488 nm argon ion laser (50 mW) as excitation source, diffraction grating having $2400\text{ lines mm}^{-1}$, an edge filter and a Peltier cooled CCD detector. Measurements were carried out at room temperature in an un-polarized mode and in the wave number range of 30 to 1000 cm^{-1} at a spectral resolution of 1 cm^{-1} .

RESULTS AND DISCUSSION

XRD patterns of samples are shown in Figure 1. The absence of sharp peaks and a broad hump at $\sim 27^\circ$ confirms the amorphous nature of the vanadium tellurite glasses.

From density measurements (Figure 2), it is observed that, as the vanadium oxide content increases the density of samples decreases from 5.22 g cm^{-3} to 3.96 g cm^{-3} . The linear decrease in density can be explained by the fact that the Te atoms are replaced by V atoms which have lower atomic weight(50.94 amu) compared to that of Te (127.63 amu).

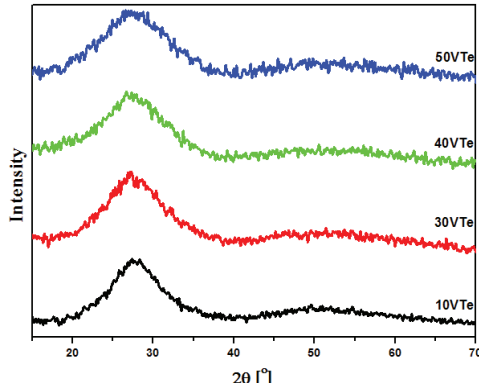


FIGURE 1. XRD patterns of V₂O₅-TeO₂ glasses.

The thermodynamic fragility is calculated as:

$$F = \frac{0.151 + \chi}{0.151 - \chi} \dots\dots\dots(1)$$

where $\chi = \frac{\Delta T_g}{T_g}$; ΔT_g is transition temperature width and it is defined as the difference between the onset point and end point. The fragility of the glasses decreases with increasing the vanadium oxide content.

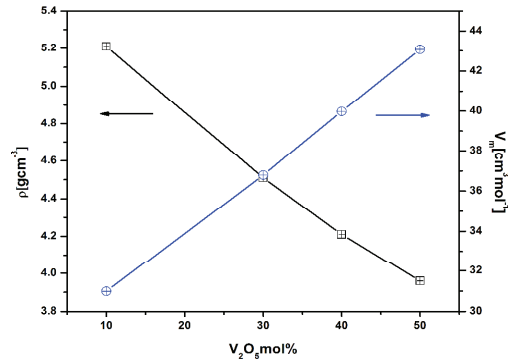


FIGURE 2. Variation of density and molar volume in V₂O₅-TeO₂ glasses with V₂O₅ mol%.

TABLE 1. Density, molar volume, DSC data and fragility index of vanadium tellurite glasses.

Sample Code	Composition (mol %)		Density [g cm ⁻³]	V _M [cm ³ mol ⁻¹]	T _g [°C]	T _c [°C]		T _m [°C]	ΔT _g	F = $\frac{0.151 + \chi}{0.151 - \chi}$
	V ₂ O ₅	TeO ₂				T _{C1}	T _{C2}			
10VTe	10	90	5.22±0.04	30.99	288	384	-	650	16	0.4624
30VTe	30	70	4.51±0.03	36.80	255	309	-	-	23	0.2521
40VTe	40	60	4.22±0.01	39.92	242	386	449	483	23	0.2259
50VTe	50	50	3.96±0.01	43.07	232	317	452	480	24	0.1871

The DSC patterns of all samples are shown in Figure 3. It is evident from DSC curves that there is one broad endothermic peak which corresponds to the transition temperature, T_g followed by an exothermic peak representing crystallization temperature T_c and as the vanadium oxide content increases, multiple crystallization peaks are observed due to the formation of different crystalline phases. From Table 1, it is clear that the value of transition temperature (T_g) of 10VTeO is 288°C (midpoint) and T_g decreases as the vanadium oxide content increases from 10 to 50 mol% although V-O linkages have higher bond enthalpy (644 kJ mol⁻¹) than Te-O (376 kJ mol⁻¹). This can be explained by considering the fact that the glass transition temperature is a function of both N_b and \bar{F} i.e

$$T_g = F(N_b, \bar{F}) \dots\dots\dots(2)$$

where \bar{F} the average force constant of the glass network and N_b is the number of bonds per unit volume of the glass. Therefore, although the average force constant \bar{F} increases, the number of network bonds per unit volume (N_b) gets decreased with increasing V₂O₅ content due to the formation of non-bridging oxygens [7]. Hence the glass transition temperature decreases from 288°C to 232°C with increasing V₂O₅ content.

Raman spectra of vanadium tellurite glasses are shown in Figure 4. The band at ~58 cm⁻¹ is the boson peak, which is a universal feature of glassy phase [8]. The spectra show the four broad bands at ~466, 663, 806 and 908 cm⁻¹. The band centered at 466 cm⁻¹ is due to bending vibration modes of Te-O-Te linkages in TeO₄ tetrahedra [2].

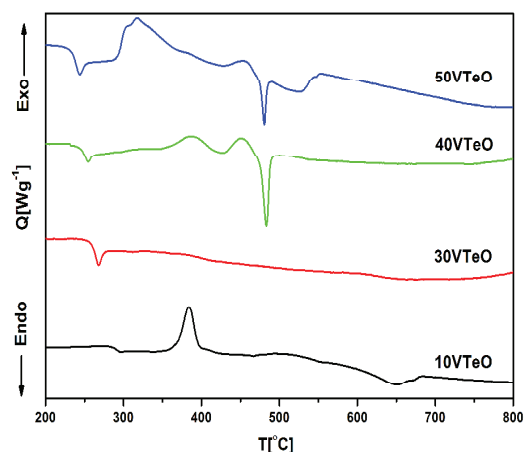


FIGURE 3. DSC patterns of V_2O_5 - TeO_2 glasses.

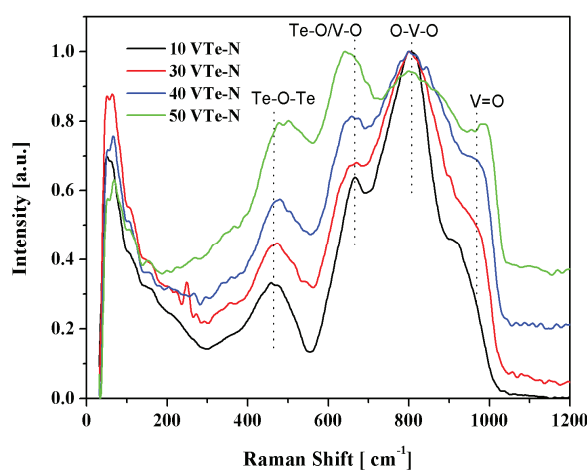


FIGURE 4. Raman spectra of V_2O_5 - TeO_2 glasses.

The peak at 663 cm^{-1} represents the Te-O/V-O vibrations, whereas the peaks at 806 cm^{-1} and 908 cm^{-1} are due to the O-V-O stretching vibrations and V=O vibrations[9]. On increasing V_2O_5 concentration from 10 to 50 mol%, there is increase in the intensity of bands at 908 cm^{-1} . The Te-O and V-O bands in Raman spectra are overlapping, hence it is not possible to determine Te-O co-ordination number from Raman studies.

CONCLUSION

V_2O_5 - TeO_2 glasses containing 10 to 50 mol% V_2O_5 were prepared by melt quenching and characterized by X-ray diffraction, density measurements, DSC and Raman studies. Glass density, glass transition temperature and the fragility index decreases with increase in V_2O_5 concentration. Glass network becomes more open with increasing V_2O_5 concentration due to the formation of non-bridging oxygens.

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