Thermal and FT-IR Properties of Semiconducting SnO₂-PbO-V₂O₅ Glass System

Ponnada Tejeswara Rao[*], Balireddy Vasundhara

Department of Physics, GITAM Institute of Technology, GITAM University, Visakhapatnam, India
Email: [*]teja_msc_phy@yahoo.co.in

Abstract

Melt quenched "SnO$_2$(50−x)PbO:50V$_2$O$_5$" glass system containing x = 5, 10, 15 in molar ratio has been investigated. Effects of heating rate, glass transition, crystallization, melting temperature and infrared spectra of SnO$_2$ substituted PbO-V$_2$O$_5$ glass system are reported. XRD results show that perfect vitrification has been achieved for all the glass samples after annealing at 150℃. DSC results have indicated that eutectic composition of the lead metavanadate has been maintained for all the glass systems up to 15 mole% of substitution. IR spectra for a SnO$_2$ substitution of 5 mole% V=O stretching frequency occur at 966 cm^{-1} without appearance of any additional peak. But for 10 mole% and 15 mole% SnO$_2$ substituted samples, additional peaks appear at 1023 and 1005 cm^{-1} indicating the effect of SnO$_2$ in the vanadate crystalline matrix such that there is an elongation of V=O bond. Since the crystalline matrix is affected, we can expect similar effect in the glass matrix also.

Keywords

1. Introduction

Transport properties of semiconducting glasses are very interesting and provide useful information on the conduction mechanisms. Modern glasses are of crucial importance for electronics and have been widely used in industry, space explorations, computer memory units, etc. IR spectroscopy is a particularly suitable method for the structural studies of vanadate system in glass and crystalline forms because of the characteristic vanadate group's

---

[*]Corresponding author.

vibrational frequencies which can be easily identified. Structural models for PbO-V$_2$O$_5$ glass systems have been discussed on the basis of IR spectroscopy [1] by comparing with those of known crystal structures. From IR and NMR spectroscopy, Hayakwa *et al.* [2] have proposed the existence of VO$_4$ tetrahedral and VO$_5$ trigonal bipyramids. The local structure around Pb in lead vanadate glasses mainly consists of PbO$_3$ trigonal and PbO$_4$ square pyramids. This study does not contradict the results obtained in earlier IR studies [3] that 50PbO:50V$_2$O$_5$ glass system contains affected VO$_5$ groups but gives additional information regarding the local environment of vanadium as well as lead ions. The lead ions are located between the vanadate chains and layers. These ions affect the isolated V=O bonds by elongating them, thus reducing their frequency. In the present studies IR spectra have been recorded in order to verify if the substituent metal oxide is replacing PbO in the glass network of the equimolar lead vanadate *i.e.*, 50PbO:50V$_2$O$_5$ glass system.
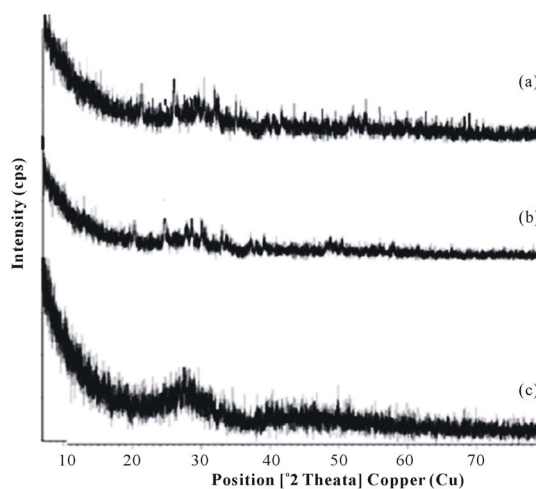
2. Experimental

The glasses were obtained by melting a chemically pure PbO, V$_2$O$_5$ and SnO$_2$ in amounts varying from 5 to 15 mole% PbO and SnO$_2$ in glazed silica crucibles in the 800°C - 1200°C temperature range. Vitrification was achieved by rapid cooling of the melt using a roller technique. The glasses were subjected to crystallization at 380°C. The prepared samples were grounded into fine powder for X-ray, DSC and FT-IR studies. X-ray studies were carried out on a PAN Alytic X'Pert-PRO diffractrometer using CuK$_\alpha$ radiation at 1.5418Å and diffractrometer settings in the 2θ range from 10°C - 70°C by changing the 2θ with a step size of 0.020. Differential Scanning calorimetry investigation of glass specimens was performed using DuPont, USA make model 2000 DSC instrument. DSC scans were conducted using 5 - 10 mg ground as-cast glass specimens which heats up at the rate of 10°C/min between 0°C and 600°C in a platinum crucible and alumina powder was used as the reference material. The density of the glass samples was determined by the Archimedes principle, using toluene as immersion liquid. In the present studies IR spectra were recorded for both the vitreous and non-vitreous samples in order to study the effect of a different metal oxide substitution in the place of PbO in the lead metavanadate glass systems.
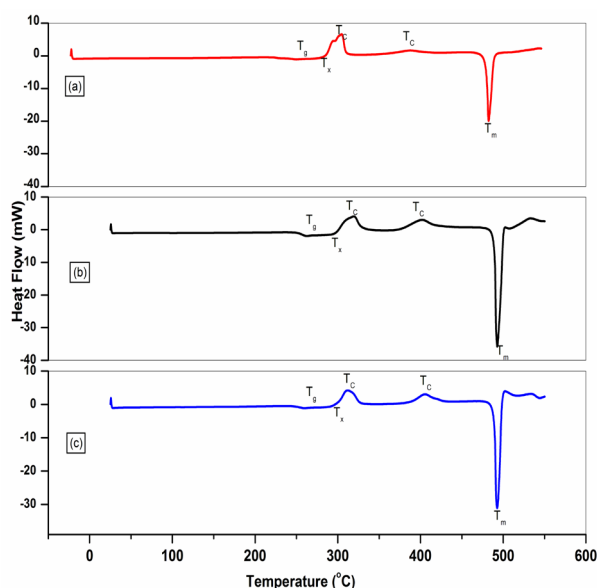
3. Results and Discussion

The X-ray diffractograms annealed at 150°C containing (x = 5, 10, 15 mole%) of SnO$_2$ showed no trace of crystallinity and are shown in **Figure 1**.

DSC investigations were conducted on the SnO$_2$-PbO-V$_2$O$_5$ glasses. The DSC patterns for these glass systems shown in **Figure 2** are slightly different when compared to the un-substituted system [4]. Values of glass transition temperature T_g, crystallization temperature T_c, melting temperature T_m, glass forming tendency K_g and densities of the xSnO$_2$(50−x)PbO:50V$_2$O$_5$ are given in **Table 1**.

Figure 1. X-ray diffractograms of xSnO$_2$(50−x)PbO: 50V$_2$O$_5$ glass system annealed at 150°C. (a) x = 5 mole%; (b) x = 10 mole%; (c) x = 15 mole%.

Figure 2. Differential scanning calorimetry curves of $xSnO_2(50-x)PbO:50V_2O_5$ glass system. (a) x = 5 mole%; (b) x = 10 mole%; (c) x = 15 mole%.

Table 1. Values of glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m) and glass forming tendency (K_g) for the $xSnO_2(50-x)PbO:50V_2O_5$.
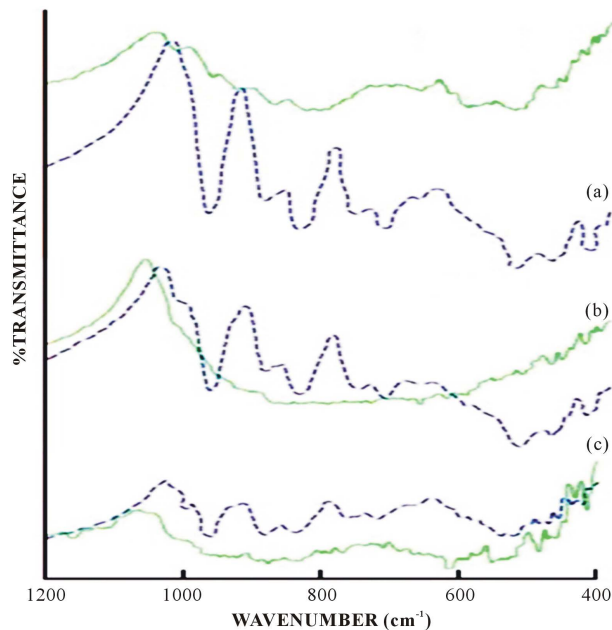
Glass Composition (mole%)			T_g (°C)	T_c (°C)	T_m (°C)	K_g	D (g/cm³)
V_2O_5 Content (mole%)	PbO Content (mole%)	SnO_2 Content (mole%)					
50	50	0	241	300,412	500	0.156	5.075
50	45	5	253	292,390	496	0.099	4.928
50	40	10	251	294,391	495	0.134	5.264
50	35	15	248	287,385	494	0.138	5.501

There is a slight change in T_g along with an increase in the number of crystallization peaks, the T_g values decrease with increasing SnO_2 contents, these results suggest that SnO_2 acts as a network modifier where as PbO acts as a network former [5]. Crystallization temperature T_c is the maximum temperature of the exotherm and onset of crystallization temperature, T_x is the beginning of the first exothermic reaction where the crystallization starts. As seen in **Figure 2** up to x = 15 mole% there is only one endothermic peak corresponding to melting point. This indicates that the substituted samples behave like the eutectic composition upto x = 15 mole%. In order to understand the devitrification tendency and thermal stability of the glass samples, glass forming tendency values K_g are calculated using the below equation.

$$K_g = \frac{T_x - T_g}{T_m - T_x} \tag{1}$$

Lower K_g suggests higher tendency of crystallization and lower thermal stability. K_g represents the temperature interval during nucleation [6]. These values indicate that the $5SnO_245PbO:50V_2O_5$ glass samples have lowest thermal stability among four compositions, with a K_g value of 0.099. The densities seem to be increasing with an increase in SnO_2 substitution. The IR spectra for the glass as well as crystalline forms are for $xSnO_2(50-x)PbO:50V_2O_5$ glass systems given in **Figure 3**. The observed IR band positions are given in **Table 2** and **Table 3**.

A consequence of disorder in the amorphous or glass systems when compared to crystalline forms is the

Figure 3. IR spectra of $xSnO_2(50-x)PbO:50V_2O_5$ glass system; ____ glass; ......crystalline. (a) x = 5 mol%; (b) x = 10 mol%; (c) x = 15 mol%.

Table 2. FT-IR data of $xSnO_2(50-x)PbO:50V_2O_5$ glass system in both amorphous and crystalline forms.

Glass Composition (mole%)				
	State	ν (V=O)	ν (VO$_2$) ν (VO$_3$)	ν (VOV)
50V$_2$O$_5$:50PbO [2]	G C	968	934 892,869,842	771 765,723
50V$_2$O$_5$:50PbO [4]	G C	964 966	885,839	770 762,720
5SnO$_2$:45PbO:50V$_2$O$_5$	G C	912 966	873,831 883,837	754,717
10SnO$_2$:40PbO:50V$_2$O$_5$	G C	966,1023	802 839,884	754,715
5SnO$_2$:35PbO:50V$_2$O$_5$	G C	941 962,1005	875,835 883,837	758,715

Table 3. FT-IR data of $xSnO_2(50-x)PbO:50V_2O_5$ glass system in both amorphous and crystalline forms.

Glass Composition (mole%)				
	State	CV	(VOV)	δ (VO$_2$, VO$_3$)
50V$_2$O$_5$:50PbO [2]	G C	646 666	574	423 534,489,434
50V$_2$O$_5$:50PbO [4]	G C	662 668	570	539,462,433 532,470,438
5SnO$_2$:45PbO:50V$_2$O$_5$	G C	667	599,532 530	478,430
10SnO$_2$:40PbO:50V$_2$O$_5$	G C	667,626	599,522 526	478,462,435 478
5SnO$_2$:35PbO:50V$_2$O$_5$	G C	617	545 538	484,412

υ (V=O) symmetric stretching, υ (VO₃) υ (VO₃) asymmetric, stretching, υ (VOV) bending frequency (symmetric and antisymmetric), C.V. combination vibration of (VO₃)ₙ single chain, G indicates glass.

breakdown of the wave vector selection (k-selection) rules, which allows electromagnetic radiation to couple with vibrations other than k = 0. As a result, unlike the crystalline case in which narrow well defined lines are observed, broad and diffuse bands representing a continuum of IR absorption result. Even though bands due to individual, localized structural units are observable, the identification of IR spectra of glasses alone is rather difficult unless crystalline spectra are also present. Hence the present discussion mainly corresponds to the IR bands observed in the devitrified samples. SnO_2 substituted samples for x = 10 and 15 mole% , there is an indication of additional bands at 1023 cm^{-1} beside 966 cm^{-1} and 1005 cm^{-1} beside 962 cm^{-1} the appearance of additional bands can be understood as the splitting of the original V=O stretching band into affected and unaffected components. The affected components arises due to the effect of dopant *i.e.* SnO_2 in the present case on V=O bond the glass matrix. In this case from the IR spectral evidence we can summarize the following.

As SnO_2 is substituted for PbO, SnO_2 is replacing PbO in the glass network in such a way that it affects V=O bond frequency, as evident by the shift in V=O band (at 1023 cm^{-1}) whose intensity increases with the increase of SnO_2 concentration. The affected V=O band (at 966 cm^{-1}) indicates the presence of meta vanadate phase containing PbO in the usual evidence we can summarize the following. As SnO_2 is substituted for PbO, SnO_2 is replacing PbO in the glass network in such a way that it affects V=O bond frequency, as evident by the shift in V=O band (at 1023 cm^{-1}) whose intensity increases with the increase of SnO_2 concentration. The affected V=O band (at 966 cm^{-1}) indicates the presence of metavanadate phase containing PbO in the usual glass network. The occurrence of the band at 1005 cm^{-1} is due to the indirect effect of SnO_2 on the V=O band in the new stable phase that is being formed. In $x(TiO_2):(100-x)(V_2O_5)$ glass containing x = 20 mole%, Dimitriev *et al.* [3] reported that the isolated V=O band is unaffected at 1020 cm^{-1}. It was observed by Dimitrov *et al.* [1] that in the IR spectra of $xPbO:(1-x)V_2O_5$ glass systems as x is varied from 0 to 75 mole% , there appears a new band in the range 970 - 955 cm^{-1} beside 1020 cm^{-1} band. It has been suggested that [3] Pb^{2+} ions occupy a position between the V-O-V layers. They exercise a direct influence of the isolated V=O bonds of VO_5 groups according to the scheme $Pb^{2+}...O=V^{5+}$. This causes an elongation of the affected V=O bond and a decrease in the vibrational frequency to 970 - 950 cm^{-1}. There may be unaffected V=O bonds whose vibrational frequency is still around 1020 cm^{-1}. With the increase of PbO, their number decreases and for eutectic composition $50PbO:50V_2O_5$ (*i.e.* PbV_2O_6 metavanadate) only one type of VO_5 polyhedron results as is evidenced by the presence of a single high frequency band in the region 955 - 970 cm^{-1} [7]. This band is observed at 966 cm^{-1} in $5SnO_2:45PbO:50V_2O_5$ system. As SnO_2 concentration is increased to 10 mol% and 15 mole%, the appearance of 1023 cm^{-1} band indicates that SnO_2 is replacing PbO in such a way that the V=O bond in the glass network of the eutectic composition is elongated [8].

4. Conclusion

Perfect vitrification has been achieved for all the glass samples as can be seen from their X-ray diffractograms of the prepared samples after annealing at 150°C for two hours. DSC recordings show that eutectic composition of the lead metavanadate has been maintained for all the glass systems up to 15 mole% of substitution. The DSC data also indicate that all the glass systems are characterized by more than one crystallization peak. This can be thought as an evidence for the existence of more than one meta-stable phase in the glass systems. The dopant SnO_2 is not divalent oxide like PbO. Besides SnO_2 is known to be glass former unlike PbO which is replacing PbO in the glass network in such a way that the eutectic composition is maintained. In the present studies the IR spectra of SnO_2 substituted samples of 5 mole% V=O stretching frequency occur at 966 cm^{-1} without the appearance of any additional peak. But for 10 mole% and 15 mole% SnO_2 substituted samples, additional peaks appear at 1023 and 1005 cm^{-1} indicating the effect of SnO_2 in the vanadate crystalline matrix such that there is an elongation of V=O bond. Since the crystalline matrix is affected, we can expect similar effect in the glass matrix also.

References

[1] Dimitrov, V. and Dimitriev, Y. (1990) Structure of Glasses in $PbO-V_2O_5$ System. *Journal of Non-Crystalline Solids*, **122**, 133-138. http://dx.doi.org/10.1016/0022-3093(90)91058-Y

[2] Hayakawa, S., Yoko, T. and Sakka, S. (1995) IR and NMR Structural Studies on Lead Vanadate Glasses. *Journal of Non-Crystalline Solids*, **183**, 73-84. http://dx.doi.org/10.1016/0022-3093(94)00652-0

[3] Dimitrov, V. (1995) Structural Changes in Vitreous Vanadate Systems. *Journal of Non-Crystalline Solids*, **192**, 183-

186. http://dx.doi.org/10.1016/0022-3093(95)00349-5

[4] Ramesh, K.V. (2000) Thermal, Electrical and Spectroscopic Studies of CuO, ZnO and TiO_2 Substituted for PbO in Eutectic Lead Vanadate Glass System. Ph.D. Thesis, Andhra University, Visakhapatnam.

[5] Oz, B., Kabaci, I., Ovecoglu, M.L. and Ozen, G. (2007) Thermal Properties and Crystallization Behavior of Some TeO_2-K_2O Glasses. *Journal of the European Society*, **27**, 1823-1827.

[6] Murugan, G.S. and Ohishi, Y.J. (2004) TeO_2-BaO-SrO-Nb $_2O_5$ Glasses: A New Glass for Waveguide Device Applications. *Journal of Non-Crystalline Solids*, **341**, 86-92. http://dx.doi.org/10.1016/j.jnoncrysol.2004.04.006

[7] Tejeswara Rao, P. (2013) Preparation and Characterization of Some Lead Meta Vanadate Semi-Conducting Glass Systems with GeO_2, Bi_2O_3 and SnO_2 Substituted for Lead Oxide. Ph.D. Thesis, Andhra University, Visakhapatnam.

[8] Tejeswara Rao, P., Ramesh, K.V. and Sastry, D.L. (2012) Electrical and Spectroscopic Studies of the CdO Substituted Lead Vanadate Glass System vs Crystalline Form. *New Journal of Glass and Ceramics*, **2**, 34-40. http://dx.doi.org/10.4236/njgc.2012.21006