

Original Research Paper

ESR and FT-IR Studies on GeO₂ Substituted Lead Vanadate Semiconducting Glass System

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Abstract: A series of Germania-lead-vanadium pentoxide glasses with $x=5, 10$ and 15 mol% were prepared by melt quenching technique and they were characterized by X-ray diffraction (XRD), Differential scanning calorimetry (DSC), Fourier Transform Infrared (FT-IR) and Electron Spin Resonance (ESR) techniques. X-ray diffraction results reveal that all samples are perfect amorphous in nature. Differential scanning calorimetry results indicate that the substituent GeO₂ is replacing PbO in the glass network in such a way that the eutectic composition is maintained. The Fourier Transform Infrared spectra characterized V=O stretching frequency around 968 cm^{-1} upto 15 mole% and interestingly the Electron Spin Resonance studies did not yield well resolved hyperfine structure due to exchange broadening which varies with nature of dopant. The Hruby parameter (K_g) for this glass system has been evaluated and reported.

Keywords: XRD, DSC, FT-IR, ESR, Semiconducting Glasses

Introduction

Glasses having Transition Metal Ions (TMIs) such as vanadium or iron ions show a semiconducting behavior. Mott (1968; 1967) found that the dc electrical conductivity of semiconducting oxide glasses is due to small polaron hopping from a low valance state to a high valance state one of a Transition Metal Ion (TMI) (e.g. from V^{4+} to V^{5+}). These glasses have been considered as a new branch in semiconducting glasses because of their wider glass forming region and possible technological applications (Saddeek *et al.*, 2009; Desoky, 2003; Shahrani *et al.*, 2003; El-Desoky *et al.*, 2005; Desoky *et al.*, 2004). In the last three decades several attempts were made to develop fast ion conducting glasses because of their prospective applications such as high energy density batteries (Takahashi *et al.*, 2010). The physical properties of the lead vanadate glasses can be improved by the addition of metal oxides (Kiran *et al.*, 2011; Kim *et al.*, 2011). Glasses containing rare earth and transition metal ions have been widely studied using structural and optical spectroscopy due to their many potential applications, like optical amplifiers in telecommunication (Pisarski *et al.*, 2005), phosphorescence materials and electrochemical batteries (Tejeswara Rao *et al.*, 2014). Of these, the PbO-V₂O₅ glass systems are receiving increased attention because of their ease of preparation. It is well known that the relationship between structure, properties and composition is one of the most important aspects of

material science. In the case of tellurite glasses the free electron pair in TeO₄ polyhedra plays an important role in the tendency to vitrify pure TeO₂. The vitrification may be facilitated by introducing new structural units compatible with the TeO₄ groups or by partly transforming TeO₄ into TeO₃ groups and by creating nonbridging bonds in the network introducing modifiers (Dimitriev *et al.*, 1979). The present investigation is to study the structure of leadvanadate glasses and it is concerned with structural role of GeO₂ in (50-x) PbO: 50V₂O₅ glass system and results are reported.

Experimental

The glasses were obtained by melting chemically pure PbO (99.9% purity, Loba Chemie, India), V₂O₅ (99.9% purity, Loba Chemie, India) and GeO₂ (99.9% purity, Loba Chemie, India) in amounts varying from 5 to 15 mole% PbO in glazed silica crucible in the 800-1200°C temperature range. The melts, which were periodically stirred to achieve homogeneous mixing, were then quenched in air at room temperature on a large stainless steel block containing 3mm diameter hole. The amorphous state of glasses was proved by X-ray diffraction using PAN alytic X'Pert-PRO diffractometer utilizing Cu K_α radiation and curved graphite monochromator. Differential scanning calorimetry recordings of the powdered glass samples were recorded with the help of a DuPont, USA make model 2000. The Infrared spectra of the glasses were recorded at room

temperature 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 using SHIMADZU Fourier Transform Infrared Spectrometer. Electron spin resonance spectra were recorded using JEOL (FE-3X) Electron spin resonance Spectrometer operated at X-band (9.3 GHz) and employing at 100 KHz field modulation.

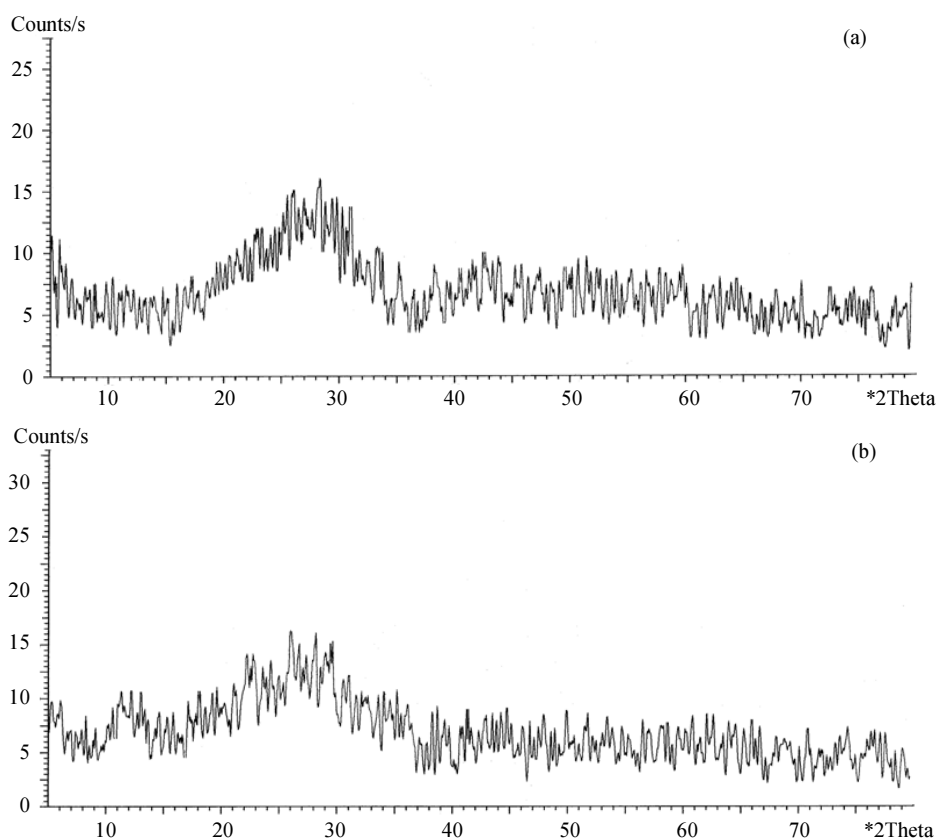
Results

The X-ray diffractograms of the present glass system ($x = 5, 10, 15$ mol%) annealed at 150°C are shown in Fig. 1. The X-ray diffraction patterns of GeO_2 doped lead vanadate glasses shows no peaks, which indicate the amorphous nature of the glass samples. The Differential scanning calorimetry patterns of the present glass system shown in Fig. 2 and calculated values of transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m) and Hruby parameter called glass forming tendency (K_g) are given in Table 1. In the Differential scanning calorimetry patterns up to $x = 15$ mole% there is only one endothermic peak corresponding to the melting point. This indicates that the substituted samples behave like the eutectic composition up to $x = 15$ mole%, the endothermic peak corresponding to melting exhibits a small shoulder when the amount of GeO_2 substitution exceeds 15 mole%. Which indicates the probability of new phases being

formed when the samples contain GeO_2 higher than 15 mole%. It can be seen from Fig. 2 that there is an increase in the number of peaks corresponding to T_c which is an indication of an increase in the number of metastable phases being formed which finally transforms to a single stable phase. In order to understand the devitrification tendency and thermal stability of the glasses, glass forming tendency values K_g are calculated using the equation given below (Kozmidis-Petrović, 2010):

$$K_g = T_x - T_g / T_m - T_x$$

According to tabulated values in Table 1 lower K_g values suggests higher tendency of crystallization and lower thermal stability. K_g represents the temperature interval during nucleation (Murugan and Ohishi, 2004). The Fourier Transform Infrared spectra of present glass system shown in Fig. 3 and the observed Fourier Transform Infrared absorption band positions are tabulated in Table 2. The present Fourier Transform Infrared studies indicate that up to $x = 15$ mol% GeO_2 replaced PbO in the $x\text{GeO}_2 (50-x) \text{PbO}: 50\text{V}_2\text{O}_5$ glass system. As can be seen from the nature of the $\text{V}=\text{O}$ band, The $\text{V}=\text{O}$ occurs around 968 cm^{-1} and does not show any splitting or significant broadening this is in agreement with Differential scanning calorimetry studies in which a single sharp melting point was observed up to $x = 15$ mol%.



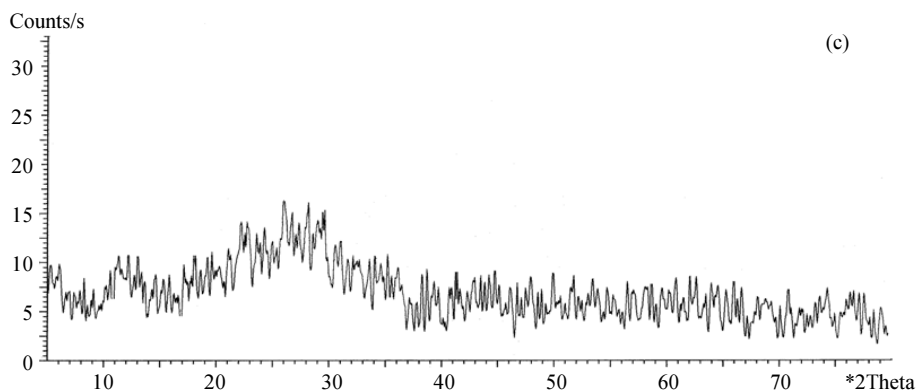


Fig. 1: X-ray diffractograms of $x\text{GeO}_2$ (50-x) $\text{PbO}:50\text{V}_2\text{O}_5$ glass system annealed at 150°C (a) $x=5$ mole% (b) $x=10$ mole% (c) $x=15$ mole%

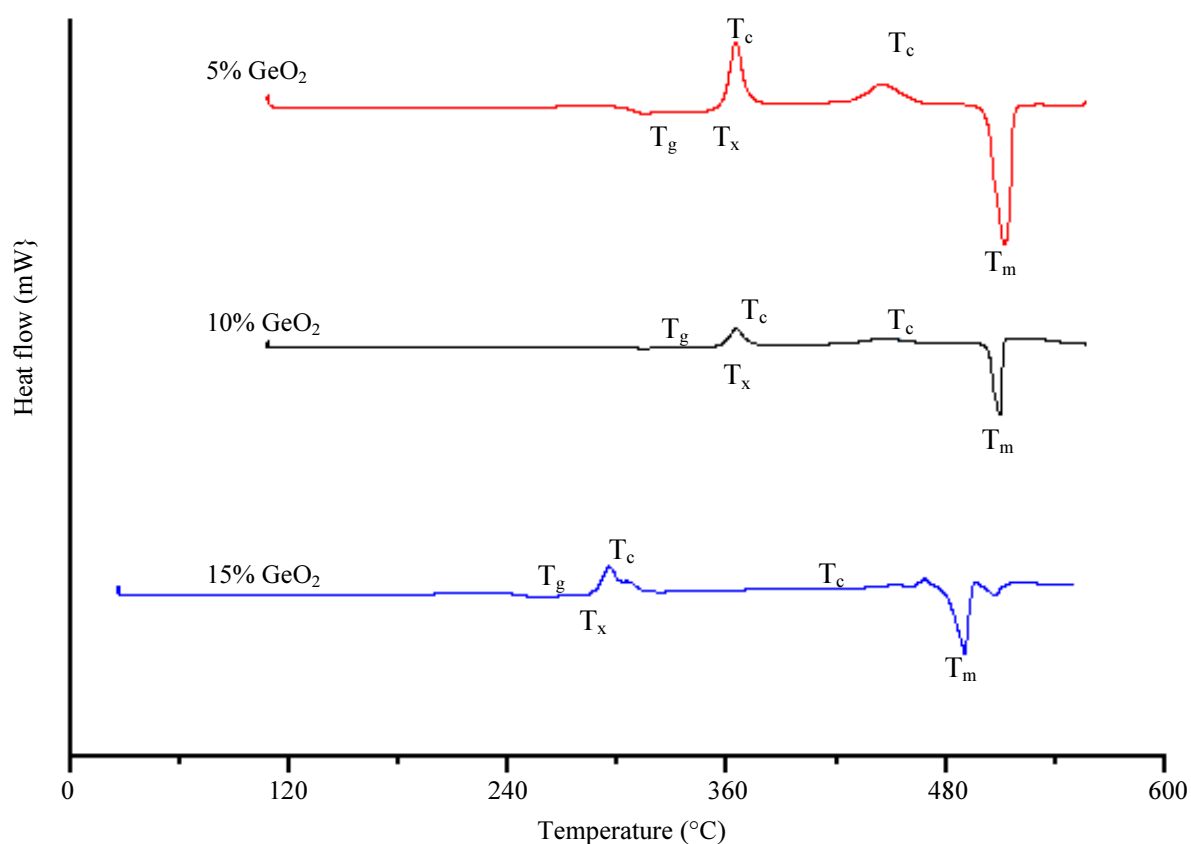


Fig. 2: Differential scanning calorimetry curves of $x\text{GeO}_2$ (50-x) $\text{PbO}:50\text{V}_2\text{O}_5$ glass system (a) $x=5$ mole% (b) $x=10$ mole% (c) $x=15$ mole%

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 $x\text{GeO}_2$ (1-x) $\text{PbO}:50\text{V}_2\text{O}_5$

Glass Composition (mole%)			Temperature ($^\circ\text{C}$)			
V_2O_5	PbO	GeO_2	T_g ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	K_g
50	50	—	241	300,412	500	0.156
50	45	5	267	327,397,420	494	0.207
50	40	10	265	325,394,419	492	0.307
50	35	15	254	295,308,388	490	0.123

Table 2: Fourier Transform Infrared spectra of $x\text{GeO}_2$ (50-x) $\text{PbO} : 50 \text{V}_2\text{O}_5$ glass system;----- glass,..... Crystalline (a) $x=5$ mol% (b) $x=10$ mol% (c) $x=15$ mol%

Composition (mole%)	State	$\nu(\text{V}=\text{O})$	$\nu(\text{VO}_2)$ $\nu(\text{VO}_2)$	$\nu(\text{VOV})$	C.V	$\nu(\text{VOV})$	$\ddot{\text{A}}(\text{VO}_2, \text{VO}_3)$
50 V_2O_5 :50 PbO (Pisarski <i>et al.</i> , 2005)	G		934	771	646		423
	C	968	892,869,842	765,723	666	574	534,489,434
5 GeO_2 :45 PbO :50 V_2O_5	G			733	669		441
	C	968	889,839	758,719	682,662,601		430
10 GeO_2 :40 PbO :50 V_2O_5	G		873	785	671	543	453,497
	C	964	877,835	756,707		528	428
15 GeO_2 :35 PbO :50 V_2O_5	G		858	750	626	522	466
	C	966	883,839	761,715		530	432

$\nu(\text{V}=\text{O})$ symmetric stretching
 $\nu(\text{VO}_2)$ $\nu(\text{VO}_3)$ asymmetric stretching
 $\nu(\text{VOV})$ bending frequency (symmetric and antisymmetric)
 C.V. combination vibration of $(\text{VO}_3)_n$ single chain
 G indicates glass
 C indicates crystalline

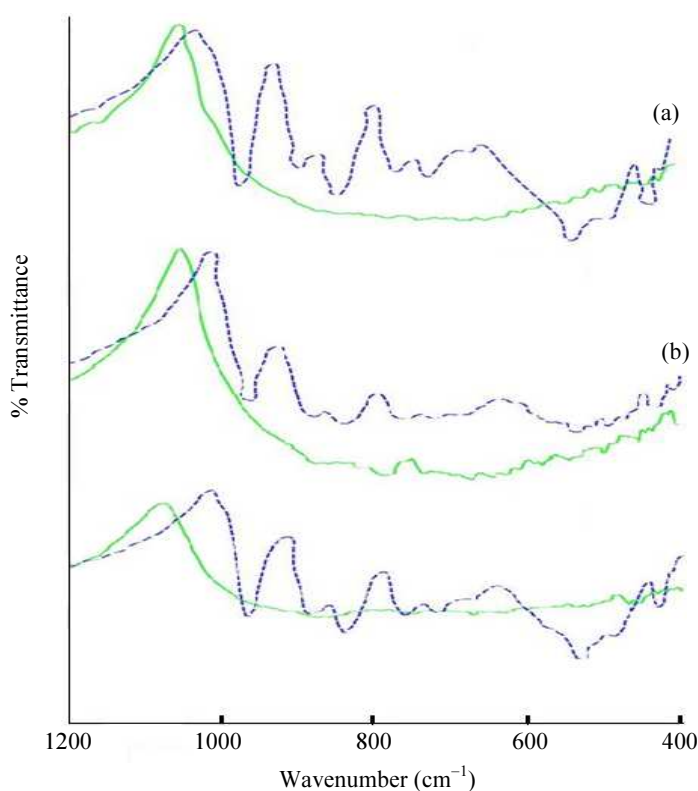


Fig. 3: Fourier Transform Infrared Spectra of $x\text{GeO}_2$ (50-x) $\text{PbO} : 50\text{V}_2\text{O}_5$ glass system; ----- glass; crystalline (a) $x=5$ mole% (b) $x=10$ mole% (c) $x=15$ mole%

In $x(\text{TiO}_2) : (100-x)(\text{V}_2\text{O}_5)$ glass containing $x = 20$ mole%, Dimitriev and Lakov (2001) reported that the isolated $\text{V}=\text{O}$ band is unaffected at 1020cm^{-1} . It was observed by Dimitrov and Dimitriev (1990) that in the Infrared spectra of $x \text{PbO} : (1-x) \text{V}_2\text{O}_5$ glass systems as x is varied from 0 to 75 mole%, there appears a new band in the range $970-955 \text{cm}^{-1}$ besides 1020cm^{-1} band. It has been suggested that (Dimitriev *et al.*, 1983) Pb^{2+} ions occupy a position between the VOV layers. They exercise a direct influence of the isolated $\text{V}=\text{O}$ bonds of

VO_5 groups according to the scheme $\text{Pb}^{2+} \dots \text{O} = \text{V}^{5+}$. This causes an elongation of the affected $\text{V}=\text{O}$ bond and a decrease in the vibrational frequency to $970-950 \text{cm}^{-1}$. There may be unaffected $\text{V}=\text{O}$ bonds whose vibrational frequency is still around 1020cm^{-1} . With the increase of PbO , their number decreases and for eutectic composition 50 $\text{PbO} : 50\text{V}_2\text{O}_5$ (i.e., PbV_2O_6 metavanadate) only one type of V_2O_5 polyhedron results as is evidenced by the presence of a single high frequency band in the region $955-970 \text{cm}^{-1}$.

The Electron spin resonance spectra of $x\text{GeO}_2$ (50-x) $\text{PbO}: 50\text{V}_2\text{O}_5$ glass samples given in Fig. 4. Very well resolved Electron spin resonance spectra observed in the $50\text{V}_2\text{O}_5:50 \text{ PbO}$ glass system (Ramesh, 2000). However such well resolved spectra could not be observed in the glass systems $x\text{GeO}_2: (1-x) \text{PbO}: \text{V}_2\text{O}_5$. A broad Electron spin resonance line with line width $\Delta H \approx 219 \text{ G}$ and having a g value ≈ 1.97 is observed for all the compositions (i.e., $x = 5, 10, 15 \text{ mol\%}$). Since parallel features could not be observed g_{\parallel} or A_{\parallel} could not be determined. Similarly A_{\perp} features could not be seen. However g_{\perp} values could be estimated and these values are given in Table 3. The collapse of the hyperfine structure can be attributed to faster electron hopping between various V^{4+} ion sites. The Electron spin resonance spectra of the present glass system i.e., $x\text{GeO}_2$ (50-x) $\text{PbO}: 50\text{V}_2\text{O}_5$ is characterized by broadening of the hyperfine lines when compared to un doped $50\text{V}_2\text{O}_5: 50 \text{ PbO}$ glass system in which well resolved hyper fine lines could be seen.

The earlier Electron spin resonance studies in ZnO , TiO_2 substituted for PbO in Lead vanadate glass system (Ramesh, 2000) and $\text{Ag}_2\text{O}, \text{CdO}$ and TeO_2 substituted for PbO in lead vanadate glass systems (Bhujangarao, 2005) relatively well resolved vanadium hyperfine structure could be seen. However, in $x \text{ CuO} (50-x)\text{PbO}:50\text{V}_2\text{O}_5$ ($x = 5, 10, 15 \text{ mole\%}$) glass system such well resolved

hyperfine structure could not be seen (Ramesh and Sastry, 2006) and this was attributed dipolar interaction between Cu^{2+} and VO^{2+} ions. However the broadening and consequent smearing out of hyperfine interaction in the present case is interesting. In the devitrified leadvanadate glass samples hyperfine interaction could not be seen and this is attributed to increased conductivity in these systems which is a result of increased hopping of electron (polaron) from one VO^{2+} site to another. This can be considered as an exchange interaction between two paramagnetic sites. As the exchange interaction increases it initially causes broadening of the ESR lines and at moderate frequencies exchange broadening takes place.

As the exchange increases hyperfine interaction and other dipolar interactions are smeared out and are exchange narrowed line. In the present case there is an exchange broadening taking place which smears out the hyperfine interaction to a large extent. In Bi_2O_3 Substituted leadvanadate glasses Rao *et al.* (2016) observed exchange broadening spectra because of high V^{4+} ion concentration. But as V^{4+} ion concentration is decreased by increased annealing of the samples better resolved Electron spin resonance spectra were observed. Mkami *et al.* (1997) studied the Electron spin resonance spectra of V^{4+} ion in the form of VO^{2+} radical in $(\text{B}_2\text{O}_3)_{1-x} (\text{V}_2\text{O}_5)_x$ glasses.

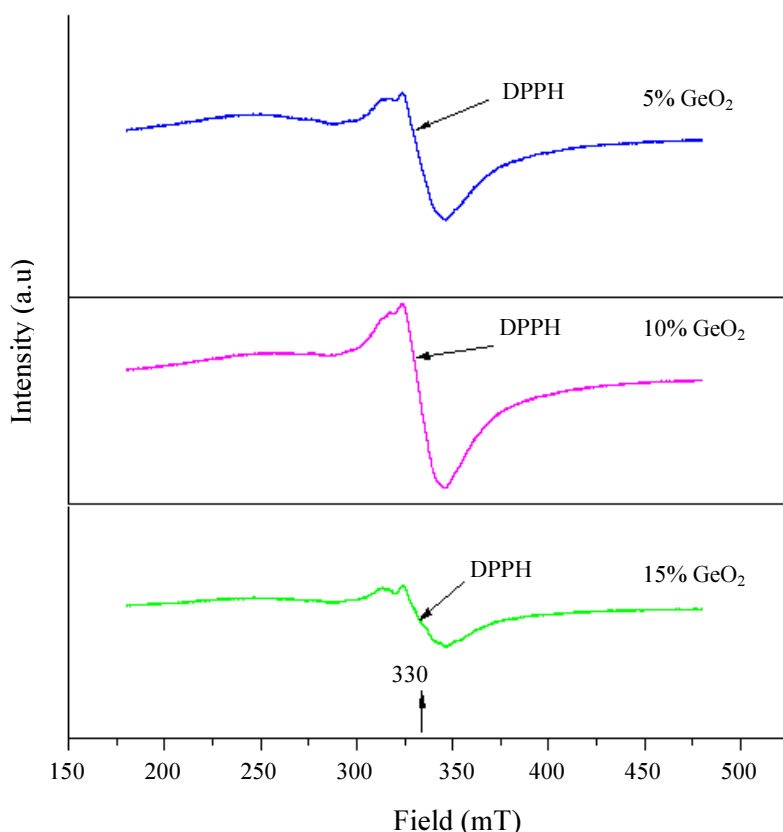


Fig. 4: Electron spin resonance spectra of $x\text{GeO}_2$ (50-x) $\text{PbO}: 50\text{V}_2\text{O}_5$ glass system at 300 K (a) $x = 5 \text{ mol\%}$ (b) $x = 10 \text{ mol\%}$ (c) $x = 15 \text{ mol\%}$

Table 3: Electron spin resonance Parameters of xGeO₂: (1-x) PbO: V₂O₅ glass system at 300K

Glass composition (mole%)			g values		Line width ΔH (G)
GeO ₂	Pbo	V ₂ O ₅	g	g _⊥	
5	45	50	-----	1.97	219
10	40	50	-----	1.96	219
15	35	50	-----	1.98	219

The obtained well resolved hyperfine lines for small values of x. But as x is increased to 0.9 they observed broadening of hyperfine lines due to exchange interaction. Livage *et al.* (1977) studied Electron spin resonance spectra of V₂O₅P₂O₅ glass system. They observed that with increase of V₂O₅ concentration the Electron spin resonance spectra are broadened and hyperfine features could not be seen. They observed that hopping frequency increases as (i) The temperature of the sample increases (ii) The disorder term W_D in the hopping frequency for phonon assisted hopping decreases. Hence we can assume that V⁴⁺ ion concentrations in the present case may be high when compared to those present in the 50PbO:50V₂O₅ sample (Ramesh, 2000). Hence the exchange broadening may be attributed to increased V⁴⁺ ion concentration in these compounds.

Conclusion

Perfect vitrification has been achieved for all the glass samples as can be seen from their X-ray diffractograms of the as prepared samples after annealing at 150°C for two hours. Differential scanning calorimetry recordings show that eutectic composition of the lead meta Vanadate has been maintained for all the glass systems upto 15 mole% of substitution. Only in the case of 15 mole% GeO₂ substituted samples there is a tendency for deviation from eutectic melting as is evidenced by the appearance of a small shoulder above the peak corresponding to eutectic melting in its Differential scanning calorimetry thermogram. The Differential scanning calorimetry data also indicates that all the glass systems are characterized by more than one crystallization peak. This can be thought that of as an evidence for the existence of more than one meta stable phase in the glass systems. In the present studies Fourier Transform Infrared spectra of GeO₂ substituted lead vanadate glass systems are characterized V = O stretching frequency around 968 cm⁻¹ upto 15 mol% substitution. Electron spin resonance spectra did not yield well resolved hyperfine structure even though these substituents are diamagnetic. The reason for the loss of resolution of hyperfine structure in the present case is attributed to exchange broadening which seems to be varying with the nature of the dopant. Hence it is presumed in the absence of V⁴⁺ estimation in the present studies that the exchange broadening of Electron spin resonance spectra of the GeO₂ substituted glass systems

are due to the increased electron hopping from one vanadium site to another (V⁴⁺ to V⁵⁺) but not due to any increase in V⁴⁺ ion concentration.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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