Semiconducting Glass System

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 V⁴⁺ to V⁵⁺). 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-V⁴⁺O glasses 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 Kα 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 using a Perkin-Elmer make model 2000 infrared spectrometer.
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):

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

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 xGeO$_2$ (50-x) PbO: 50V$_2$O$_5$ glass system. As can be seen from the nature of the V = O band, the V=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%.

![Graph](a)

![Graph](b)
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 system.

| Glass Composition (mole%) | Temperature (°C) | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $K_g$ |
|---------------------------|------------------|------------|------------|------------|-------|
| $\text{V}_2\text{O}_3$ | $\text{PbO}$ | $\text{GeO}_2$ |             |            |       |
| 50                         | 50               | 5          |            |            |       |
| 50                         | 45               | 10         |            |            |       |
| 50                         | 35               | 15         |            |            |       |
Table 2: Fourier Transform Infrared spectra of xGeO$_2$ (50-x) PbO: 50 V$_2$O$_5$ glass system; ----- glass, ...... Crystalline (a) x=5 mol% (b) x=10 mol% (c) x=15 mol%

| Composition (mole%) | State | i(V = 0) | i(VO$_2$)(VO$_3$) | i(VOV) | C.V. | i(VOV) | A(VO$_2$VO$_3$) |
|---------------------|-------|----------|-------------------|--------|------|--------|-----------------|
| 50V$_2$O$_5$:50PbO (Pisarski et al., 2005) | G     | 934      | 771               | 646    | 423  |
|                     | C     | 968      | 892,869,842       | 765,723| 666  | 574    | 534,489,434    |
| 5GeO$_2$:45PbO:50V$_2$O$_5$ | G     | 968      | 733               | 669    | 543  | 441    |
|                     | C     | 968      | 889,839           | 758,719| 682,662,601| 430  |
| 10GeO$_2$:40PbO:50V$_2$O$_5$ | G     | 964      | 873               | 785    | 671  | 543    | 453,497        |
|                     | C     | 964      | 877,835           | 756,707| 528  | 428    |
| 15GeO$_2$:35PbO:50V$_2$O$_5$ | G     | 966      | 858               | 750    | 626  | 522    | 466            |
|                     | C     | 966      | 883,839           | 761,715| 530  | 432    |

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

![Fourier Transform Infrared Spectra of xGeO$_2$ (50-x) PbO: 50V$_2$O$_5$ glass system; ----- glass; ...... crystalline (a) x=5 mole% (b) x=10 mole% (c) x=15 mole%](image)

In x (TiO$_2$): (100-x) (V$_2$O$_5$) glass containing x = 20 mole%, Dimitriev and Lakov (2001) reported that the isolated V = O band is unaffected at 1020 cm$^{-1}$. It was observed by Dimitrov and Dimitriev (1990) that in the Infrared spectra of x PbO: (1-x) V$_2$O$_5$ glass systems as x is varied from 0 to 75 mole%, there appears a new band in the range 970-955 cm$^{-1}$ besides 1020 cm$^{-1}$ 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 V = O bonds of VO$_3$ 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 50 PbO:50V$_2$O$_5$ (i.e., PbV$_2$O$_6$ metavanadate) only one type of V$_2$O$_5$ polyhedron results as is evidenced by the presence of a single high frequency band in the region 955-970 cm$^{-1}$. 

![Graph showing % Transmittance vs Wavenumber (cm$^{-1}$)](image)
The Electron spin resonance spectra of xGeO$_2$ (50-x) PbO: 50V$_2$O$_5$ glass samples given in Fig. 4. Very well resolved Electron spin resonance spectra observed in the 50V$_2$O$_5$:50 PbO glass system (Ramesh, 2000). However such well resolved spectra could not be observed in the glass systems xGeO$_2$: (1-x) PbO: V$_2$O$_5$. A broad Electron spin resonance line with line width $\Delta H\approx 219$ G and having a g value $\approx 1.97$ is observed for all the compositions (i.e., $x = 5, 10, 15$ mol%). Since parallel features could not be observed $g_{||}$ or $A_{||}$ 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., xGeO$_2$ (50-x) PbO: 50V$_2$O$_5$ is characterized by broadening of the hyperfine lines when compared to un doped 50V$_2$O$_5$: 50 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 Ag$_2$O,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 CuO (50-x) PbO:50V$_2$O$_5$ ($x = 5,10,15$ 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$_2$O$_3$ 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 (B$_2$O$_3$)$_{1-x}$ (V$_2$O$_5$)$_x$ glasses.

![Electron spin resonance spectra of xGeO$_2$ (50-x) PbO: 50V$_2$O$_5$ glass system at 300 K](image)

**Fig. 4:** Electron spin resonance spectra of xGeO$_2$ (50-x) PbO: 50V$_2$O$_5$ glass system at 300 K (a) $x = 5$ mol% (b) $x = 10$ mol% (c) $x = 15$ mol%
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 W₀ 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 mol% substitution. Only in the case of 15 mol% 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.

**References**

Blujangarao, C., 2005. New Results in the electrical, thermal and spectroscopic investigations of lead metavanadate glass system modified byAg₂O, CdO and TeO₂ substitutions. PhD Thesis, Andhra University, Visakhapatnam, India.

Desoky, E.M.M., 2003. Small polaron transport in V₂O₅–NiO–TeO₂ glasses. J. Materials Sci. Materials Electronics, 14: 215-221.

Desoky, E.M.M., A. Hajry and M. Tokunaga, 2004. Effect of sulfur addition on the redox state of iron in iron phosphate glasses. Hyperfine Interact., 156: 547-553.

Dimitriev, Y. and L. Lakov, 2001. The structure of oxide glasses containing SeO₂. J. Non-Crystalline Solids, 293: 410-415.

Dimitriev, Y., V. Dimitrov and M. Arnaudov, 1979. Infra-red spectra of crystalline phases and related glasses in the TeO₂–V₂O₅–Me₂O system. J. Materials Sci., 14: 723-727. DOI: 10.1007/BF00772736

Dimitriev, Y., V. Dimitrov, M. Arnaudov and D. Topalov, 1983. IR-spectral study of vanadate vitreous systems. J. Non-Crystalline Solids, 57: 147-156. DOI: 10.1016/0022-3093(83)90417-9

Dimitriev, V. and Y. Dimitriev, 1990. Structure of glasses in PbO-V₂O₅ system. J. Non-Crystalline Solids, 122: 133-138.

El-Desoky, M.M., N.M. Tashtoush and M.H. Habib, 2005. Characterization and electrical properties of semiconducting Fe₂O₃–Bi₂O₃–K₂B₂O₇ glasses. J. Materials Science: Materials Electronics, 16: 533-539.

Kim, C.E., H.C. Hwang, M.Y. Yoon, B.H. Choi and H.J. Hwang, 2011. Fabrication of a high lithium ion conducting lithium borosilicate glass. J. Non-Crystalline Solids, 357: 2863-2867. DOI: 10.1016/j.jnoncrysol.2011.03.022

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

| Glass composition (mole%) | Glass composition | GeO₂ | PbO | V₂O₅ | g values | Line width | ΔH (G) |
|--------------------------|------------------|------|-----|------|----------|-----------|--------|
|                          |                  | 5    | 45  | 50   | --------- | 1.97      | 219    |
|                          |                  | 10   | 40  | 50   | --------- | 1.96      | 219    |
|                          |                  | 15   | 35  | 50   | --------- | 1.98      | 219    |
Kiran, N., C.R. Kesavulu, A.S. Kumar and J.L. Rao, 2011. Spectral studies on Mn\(^{2+}\) ions doped in sodium-lead borophosphate glasses. Physica B: Condensed Matter, 406: 3816-3820. DOI: 10.1016/j.physb.2011.06.078

Kozmidis-Petrović, A.F., 2010. Theoretical analysis of relative changes of the Hruby, Weinberg, and Lu–Liu glass stability parameters with application on some oxide and chalcogenide glasses. Thermochimica Acta, 499: 54-60.

Livage, J., P. Pineau, M.C. Leroy and M. Michaud, 1977. Semiconducting vanadium phosphate glasses. Phys. Status Solidi, 39: 73-78. DOI: 10.1002/pssa.2210390107

Mkami, E.H., B. Deroide, N. Abidi, P. Rumori and J.V. Zanchetta, 1997. ESR study and dc conductivity of binary glasses of the system (V\(_2\)O\(_5\)) \(_x\) (B\(_2\)O\(_3\)) \(_{1-x}\). Phys. Chem. Glasses, 38: 137-143.

Mott, N.F., 1967. Electrons in disordered structures. Advances Phys., 50: 49-144. DOI: 10.1080/00018730110102727

Mott, N.F., 1968. Conduction in glasses containing transition metal ions. J. Non-Crystalline Solids, 1: 1-17. DOI: 10.1016/0022-3093(68)90002-1

Murugan, G.S. and Y. Ohishi, 2004. TeO\(_2\)–BaO–SrO–Nb\(_2\)O\(_5\) glasses: A new glass system for waveguide devices applications. J. Non-Crystalline Solids, 341: 86-92.

Pisarski, W.A., T. Goryczka, B. Wodecka-Duś, M. Plotiska and J. Pisarska, 2005. Structure and properties of rare earth-doped lead borate glasses. Materials Sci. Eng., B, 122: 94-99.

Ramesh, K.V. and D.L. Sastry, 2006. IR and ESR studies of CuO substituted for PbO in eutectic lead vanadate glass system. J. Non-Crystalline Solids, 352: 5421-5428.

Ramesh, K.V., 2000. Thermal, electrical and spectroscopic studies of CuO, ZnO and TiO\(_2\) substituted for PbO in eutectic lead vanadate glass system. Thesis PhD. Andhra University, Visakhapatnam.

Rao, P., D. Tejeswara, L. Sastry and K.V. Ramesh, 2016. ESR and dc electrical properties of Bi\(_2\)O\(_3\)–PbO–V\(_2\)O\(_5\) glass system. Phys. Chem. Glasses-European J. Glass Sci. Technol. Part B, 57: 279-284.

Saddeek, Y.B., E.R. Shaaban, K.A. Aly and I.M. Sayed, 2009. Characterization of some lead vanadate glasses. J. Alloys Compounds, 478: 447-452. DOI: 10.1016/j.jallcom.2008.11.063

Shahrani, A.A., A.A. Hajry and M.M.E. Desoky, 2003. Non-adiabatic small polaron hopping conduction in sodium borate tungstate glasses. Phys. Status Solidi, 2: 378-387. DOI: 10.1002/pssa.200306689

Takahashi, H., T. Karasawa, T. Sakuma and J.E. Garbarczyk, 2010. Electrical conduction in the vitreous and crystallized Li\(_2\)O–V\(_2\)O\(_5\)–P\(_2\)O\(_5\) system. Solid State Ionics, 181: 27-32. DOI: 10.1016/j.ssi.2009.12.001

Tejeswara Rao, P., D.L. Sastry, K.V. Ramesh and B. Srinivasarao, 2014. Thermal and conductivity properties of Semiconducting SnO\(_2\)-PbO-V\(_2\)O\(_5\) glasses. Proceedings of the National Conference on Advanced Functional Materials and Computer Applications in Materials Technology, Special Edition, pp: 2321-5674.