

Optical properties of zinc–vanadium glasses doped with samarium trioxide

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Abstract. Zinc–vanadium glasses doped with samarium oxide having the chemical composition $\text{Sm}_2\text{O}_3(x)\text{ZnO}_{(40-x)}\text{V}_2\text{O}_5(60)$ (where $x = 0.1\text{--}0.5$ mol%) were prepared by melt quenching method. The density of these glasses was measured by Archimedes method; the corresponding molar volumes have also been calculated. The values of density range from 3.7512 to 5.0535 gm/cm^3 and those of molar volume range from 28.3004 to 37.6415 cm^3 . The optical absorbance studies were carried out on these glasses to measure their energy bandgaps. The absorption spectra of these glasses were recorded in UV–Visible region. No sharp edges were found in the optical spectra, which verify the amorphous nature of these glasses. The calculated optical bandgap energies of these glasses were found to be in the range of 0.3173–0.6640 eV. The refractive index and polarizability of oxide ion have been calculated by using Lorentz–Lorentz relations. The values of refractive index range from 1.1762 to 1.2901 and those of polarizability of oxide ion range from 1.6906×10^{-24} to 2.2379×10^{-24} cm^3 .

Keywords. Amorphous materials; optical properties; polarizability of oxide ion; energy bandgap.

1. Introduction

Vanadium containing oxide glasses continue to be of interest because of their unique properties and correspondingly their potential stability for applications. For example, binary and ternary V_2O_5 glasses can exhibit a semiconducting behaviour (Ghosh 1990; Livage *et al* 1990; Ichinose and Nakai 1996; Khattak *et al* 2009), which arises from an unpaired $3d^1$ electron hopping between transition metals (TM) ions (Mott 1968; Austin and Mott 1969) when TM ions exist in two or more valence state i.e. an electron hopping from V^{4+} to V^{5+} site. It is also known that V^{5+} in low ratios enter the amorphous structure as an impurity whereas V^{5+} in high ratios are present in structure as glass formers (Dawy and Salam 2001). Glasses with transitional metal ions came into prominence because of their notable spectroscopic properties and their suitability for fibre optic communications, luminescent solar energy concentrators (Muruli *et al* 2005). Vanadium based glasses have gained much interest in solid-state chemistry and materials science with regard to their possible applications as memory and switching devices (Khattak *et al* 2000; Rao and Veeraiyah 2004). Optical absorption studies on amorphous materials yield important information regarding electronic and vibrational edges plus the contributions from impurities such as transitional metal ions. Stevels (1947) was the first to suggest that the intrinsic absorption edge of an oxide glass corresponded to the transition of valence electron of an oxygen ion in the glass network to

an excited state. Although thermal vibration is assumed to be responsible for the tail part of the optical absorption edge a number of glasses obeying Urbach rule for the absorption coefficient, whose physical origin is not well understood (Shashidhar Bale and Syed Rahman 2009). Glass is a promising host to investigate the influence of chemical environment on the optical properties of the rare-earth ions. Glass activated with rare-earth ions, emitting electromagnetic waves in NIR region are of current interest because of their potential as laser host materials and optical amplifiers for use in telecommunications (Pisarski *et al* 2005; Das *et al* 2006).

Therefore, the aim of the present study is to investigate the effect of Sm_2O_3 content on optical bandgap, density, molar volume, refractive index and polarizability in zinc–vanadium glasses doped with Sm_2O_3 .

2. Theory

The absorption coefficient $\alpha(\nu)$ in amorphous materials, in the optical region near the absorption edge at particular temperature, obeys empirical relation known as Urbach rule (Urbach 1953) given by:

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_c), \quad (1)$$

where $h\nu$ is the photon energy, α_0 the constant and E_c the energy which is interpreted as the width of the localized state in the normally forbidden bandgap and also known as the Urbach energy.

In amorphous materials, absorption due to the band-to-band transitions that determines the optical energy gap was

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interpreted by Mott and Davis (1970) and can be written in general form:

$$\alpha(\nu) = (B/h\nu)(h\nu - E_{\text{opt}})^n, \quad (2)$$

where B is a constant and $h\nu$ the photon energy, E_{opt} the optical energy gap and n is an index which can have any values between 1/2 and 3 depending on the nature of the interband electronic transitions (Al-Ani and Higazy 1991). Goodness of the fit of the data to the formula for either $n = 1/2$ (direct bandgap) or $n = 2$ (indirect bandgap) is determined. It has been found that for many amorphous materials, a reasonable fit of (2) with $n = 2$ is achieved. This is the case of indirect transitions, where the interactions with lattice vibrations take place.

Among the theoretical expressions, the Lorentz–Lorentz equation (Rawson 1980) relates the electronic polarizability (α_m), to the refractive index (n), as follows:

$$\frac{n^2 - 1}{n^2 + 2} (V_m) = 4/3\pi N\alpha_m, \quad (3)$$

where V_m is the molar volume, N the Avogadro number and α_m the polarizability of oxide ion.

3. Experimental

3.1 Sample preparation

The glass samples having composition $\text{Sm}_2\text{O}_{3(x)}\text{ZnO}_{(40-x)}\text{V}_2\text{O}_{5(60)}$ (where $x = 0.1\text{--}0.5$ mol%) were prepared by melt quenching method. The mixtures of analytical grade vanadium pentoxide (V_2O_5), zinc oxide (ZnO) and samarium trioxide (Sm_2O_3) were used as starting materials. The detailed experimental procedure was explained in (Eraiah and Sudha 2007). The samples were annealed at 200 °C for 2 h to eliminate the mechanical and thermal stress. The amorphous nature of these glasses was examined by X-ray diffraction analysis at room temperature. Figure 1 shows X-ray diffraction spectra of all samples and showed the diffused band characteristics of X-ray diffraction pattern of amorphous materials; the spectra did not show any sharp peaks and confirms that the glass samples are amorphous in nature.

3.2 Density and molar volume

The densities of these glass samples were measured by the Archimedes method using toluene as an immersion liquid (density = 0.86 g/cm³). The corresponding molar volumes were calculated by using the relation $V_m = M/\rho$, where M is the molecular weight and ρ is the density of corresponding glass samples.

3.3 Optical absorption

The optical absorption spectra for these glasses were recorded using Hitachi-U-3200 absorption spectrophotometer

in the wavelength region 250–700 nm at normal incidence. The optical absorption coefficient $\alpha(\nu)$ was calculated for each sample at different photon energies by using the relation $\alpha(\nu) = A/d$, where A is the absorbance and ‘ d ’ is the thickness of the samples.

3.4 Refractive index

Refractive index of these glasses has been calculated by using the relation:

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{E_g/20}, \quad (4)$$

which was proposed by Dimitrov and Sakka (1996).

3.5 Electronic polarizability

The most important properties of materials, which are closely related to their applicability in the field of optics and electronics is electronic polarizability; it is therefore, of importance to estimate electronic polarizabilities of glasses. So far, since the pioneering many works or the approach for the electronic polarizability of glasses and materials have been reported by various authors (Dimitrov and Kamatsu 2002, 2005a, b). The electronic polarizability of glasses can be evaluated by using the Lorentz–Lorentz equation, giving the relationship between the molar refraction, refractive index and density. The electronic polarizability of oxide ions for these glasses was estimated by using (3).

4. Results and discussion

The measured and calculated values of densities, molar volumes, optical energy bandgaps, refractive indices and

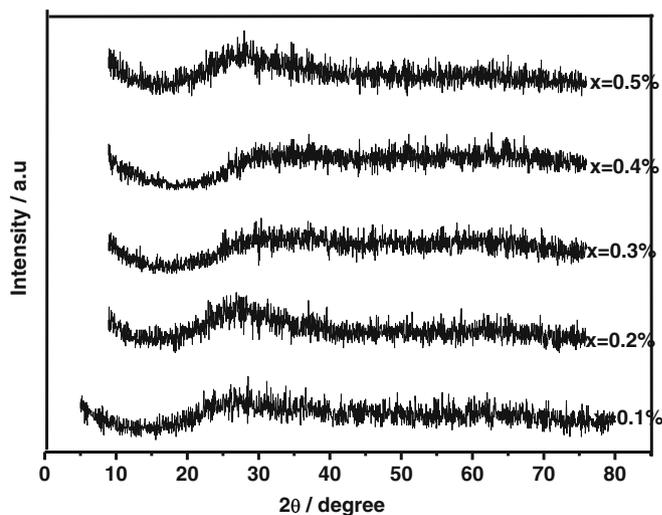
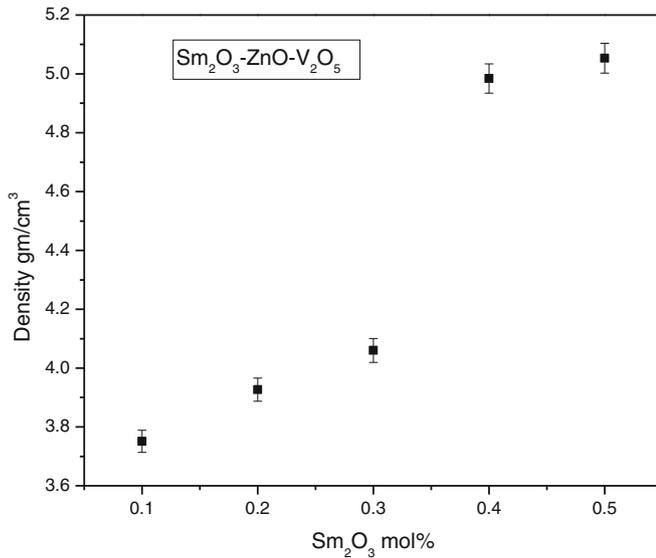


Figure 1. X-ray diffraction pattern of $\text{Sm}_2\text{O}_3\text{--ZnO--V}_2\text{O}_5$ glasses.

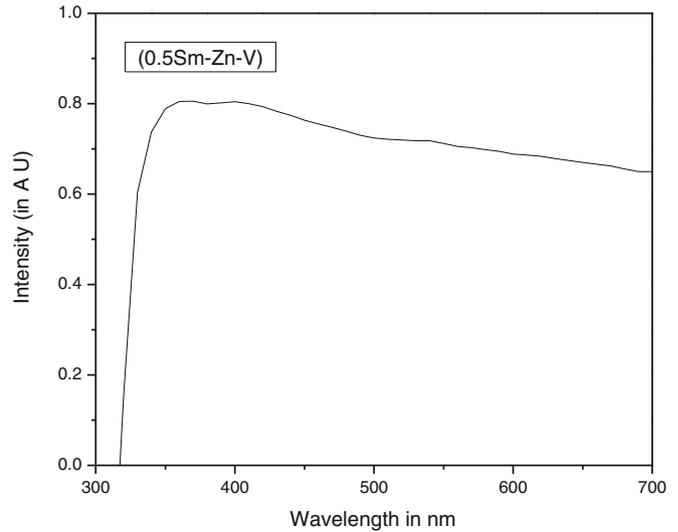
Table 1. Density, molar volume, optical energy bandgap, refractive index and electronic polarizability of oxide ion for Sm₂O₃–ZnO–V₂O₅ glasses.

Glass composition (mol%)			Density (ρ) (g/cm ³)	Molar volume (V_m) (cm ⁻³)	Energy bandgap (E_g) (eV)	Refractive index (n)	Electronic polarizability (α_e) ($\times 10^{-24}$) (cm ³)
Sm ₂ O ₃	ZnO	V ₂ O ₅					
0.1	39.9	60	3.7512	37.6415	0.6640	1.1762	1.6906
0.2	39.8	60	3.9263	36.2205	0.6160	1.2458	2.2310
0.3	39.7	60	4.0599	35.0945	0.5440	1.2551	2.2379
0.4	39.6	60	4.9844	28.6388	0.3173	1.2901	2.0578
0.5	39.5	60	5.0535	28.3004	0.5866	1.2495	1.7676

**Figure 2.** Variation of density as a function of Sm₂O₃.

polarizability of oxide ions for Sm₂O₃–ZnO–V₂O₅ glasses are listed in table 1. The variation of measured densities of these glasses with Sm₂O₃ concentration is shown in figure 2. From the figure, it can be seen that, by the addition of Sm₂O₃ into ZnO–V₂O₅ glass network, the density increases with respect to increase in mol% of Sm₂O₃. This indicates that by the addition of Sm₂O₃ into the glass network, it may resist the creation of non-bridging oxygen up to 0.4 mol% of Sm₂O₃ hence, the density increases. It can also be observed that density increases with decreasing concentration of ZnO, which act as an intermediate glass former/modifier in glass system (Dimitrov and Kamatsu 2002).

Figure 3 shows typical absorption spectrum of samarium doped zinc–vanadium glasses. The absorption coefficients, $\alpha(\nu)$, were determined near the absorption edge at different photon energies for all glass samples. It has been observed that for indirect allowed transitions, the measured absorption data fits well in (2) for $n = 2$. Therefore, the results were plotted as $(\alpha h\nu)^{1/2}$ vs photon energy ($h\nu$) a typical plot is shown in figure 4, for indirect allowed transitions to find the values of optical bandgap, E_{opt} . It can be seen that there exists a linear dependence of $(\alpha h\nu)^{1/2}$ in the photon energy

**Figure 3.** A typical absorption spectrum of Sm₂O₃–ZnO–V₂O₅ glasses.

($h\nu$). This suggests that at higher photon energies, the transitions occurring in the present glass samples are of indirect type (figure 4).

The values of the optical bandgaps obtained are listed in table 1 and are depicted in figure 5 as a function of Sm₂O₃. It can be noticed that the optical bandgap decreases with increase of Sm₂O₃ concentration up to 0.4 mol%. Further addition of Sm₂O₃ results in the slight increase in the optical bandgap. This trend of results is similar to the behaviour of density of these glasses. The dropping E_g at 0.4 mol% may be due to the variation of density as well as the variation of non-bridging oxygens. The creation of non-bridging oxygens may take place at 0.4 mol% of Sm₂O₃. In this glass system at 0.4 mol% Sm₂O₃, due to the increase in oxygen packing density, the structure becomes more compact and hence the density also increases at 0.4 mol% of Sm₂O₃ due to the dual (glass modifier and former) nature of ZnO, it act as a network modifier up to 0.4 mol%, then it may occupy network former position (Dimitrov and Kamatsu 2002).

Figure 6 shows variation of refractive index vs mol% of Sm₂O₃. As can be seen from the figure, refractive index increases gradually with increasing the concentration of Sm₂O₃ up to 0.4 mol% then the value slowly decreases

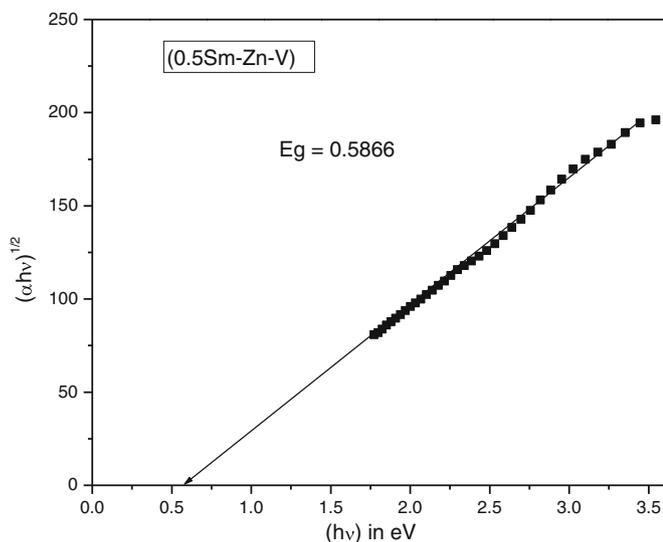


Figure 4. A typical plot of $(\alpha hv)^{1/2}$ vs photon energy (hv) .

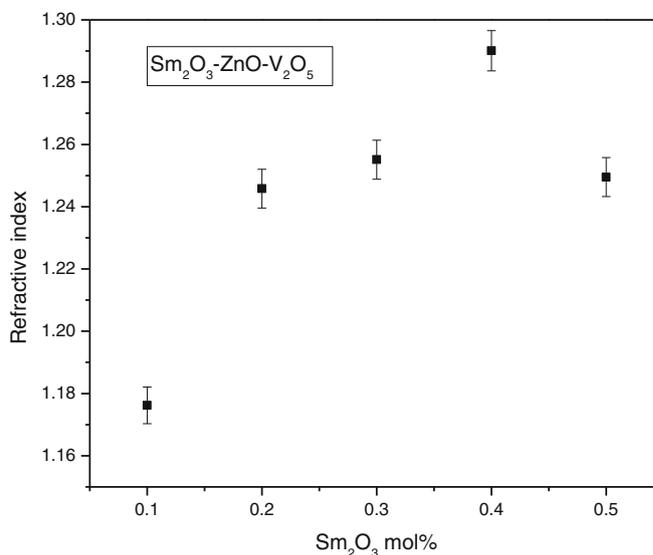


Figure 6. Variation of refractive indices vs mol% of Sm_2O_3 .

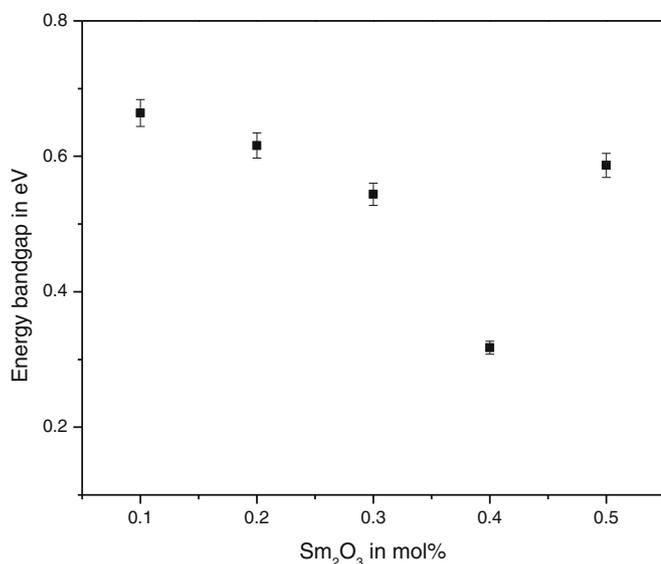


Figure 5. Variation of optical energy bandgap values vs mol% of Sm_2O_3 .

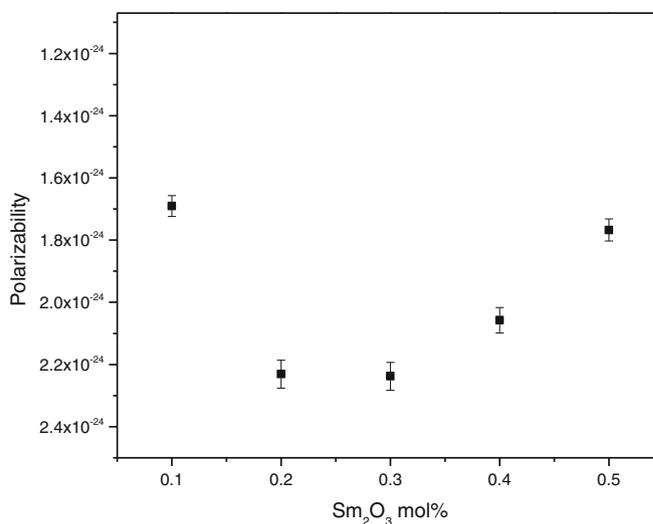


Figure 7. Variation of polarizability of oxide ions vs mol% of Sm_2O_3 .

at 0.5 mol% of Sm_2O_3 . The trend of variation is exactly opposite to the energy bandgap variation.

Figure 7 shows variation of electronic polarizability of oxide ions vs mol% of Sm_2O_3 . As can be seen from the figure electronic polarizability decreases initially up to a minimum of about 0.3 mol% then it starts increasing up to 0.5 mol% of Sm_2O_3 . This indicates that an addition of Sm_2O_3 content into $\text{ZnO-V}_2\text{O}_5$ glass network breaks bridging V–O–V bonds and new non-bridging bonds like V–O– Zn^{2+} may be formed (Ganguli *et al* 1999; Yasser *et al* 2009). The non-bridging bonds have greater ionic character and lower bond energies (Michael 1999; Balta 2005). This indicate that rare-earth doped oxide glasses have quite different electronic structure.

5. Conclusions

It has been found that, Sm_2O_3 played an important role in the glass network, by increasing the concentration of Sm_2O_3 density increases and molar volume decreases up to 0.5 mol% of Sm_2O_3 . By fixing V_2O_5 concentration, decreasing ZnO concentration leads to compaction of glass network by breaking the bonds between V–O–V allowing the formation of V–O–Zn and in this way the density of the glasses also increases. This reveals that ZnO enters the glass structure as network modifier and as well as network former. The trend of optical bandgap is similar to the behaviour of density of these glasses. However, by doping with Sm_2O_3 , the optical bandgap is constituted by the host materials, which does not alter much in the bandgap picture of the host glass. Hence,

very slight variation in refractive index and polarization of oxide ions have been observed.

References

- Al-Ani S K J and Higazy A A 1991 *J. Mater. Sci.* **26** 3670
- Austin I G and Mott N F 1969 *Adv. Phys.* **18** 41
- Balta P 2005 *J. Optoelectronics Adv. Mater.* **7** 2347
- Dawy M and Salam A H 2001 *Mater. Chem. Phys.* **71** 137
- Dimitrov V and Sakka S 1996 *J. Appl. Phys.* **79** 1736
- Dimitrov V and Kamatsu T 2002 *J. Solid State Chem.* **163** 100
- Dimitrov V and Kamatsu T 2005a *Phys. Chem. Glasses* **46** 521
- Dimitrov V and Kamatsu T 2005b *J. Solid State Chem.* **178** 831
- Eraiah B and Sudha G Bhat 2007 *J. Phys. Chem. Solids* **68** 581
- Ganguli M, Harish Bhat M and Rao K J 1999 *J. Phys. Chem. Glasses* **40** 297
- Ghosh A 1990 *Phys. Rev.* **B42** 5665
- Ichinose N and Nakai Y 1996 *J. Non-Cryst. Solids* **203** 353
- Khattak G D, Salim M A, Wenger L E and Gilani A H 2000 *J. Non-Cryst. Solids* **262** 66
- Khattak G D, Mekki A and Wenger L E 2009 *J. Non-Cryst. Solids* **355** 2148
- Livage J, Jollivet J P and Tronc E 1990 *J. Non-Cryst. Solids* **121** 35
- Maumita Das, Annapurna K, Kundu P, Dwivedi R N and Buddhudu S 2006 *Mater. Lett.* **60** 222
- Michael A Velbel 1999 *Am. J. Sci.* **299** 679
- Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
- Mott N F and Davis E A 1970 *Philos. Magn.* **28** 903
- Muruli A, Chakradhar R P S and Rao J L 2005 *Phys.* **B358** 19
- Pisarski W A, Goryczka T, Wodecka-Dus B, Plonska M and Pisarski J 2005 *Mater. Sci. Eng.* **B122** 94
- Rao R B and Veeraiah N 2004 *Physica B* **348** 256
- Rawson H 1980 *Properties and applications of glass* (Amsterdam: Elsevier)
- Shashidhar Bale and Syed Rahman 2009 *J. Non-Cryst. Solids* **355** 2127
- Stevens J M 1947 *Proc. Int. Cong. Pure Appl. Chem.* **11** 519
- Urbach F 1953 *Phys. Rev.* **92** 1324
- Yasser B Saddeek, Essam R Saaban, Kamal A Aly and Sayed I M 2009 *J. Alloys Comp.* **478** 447