

Optical properties of lead–tellurite glasses doped with samarium trioxide

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Abstract. The optical properties of a new family of $x\text{Sm}_2\text{O}_3-(40-x)\text{PbO}-60\text{TeO}_2$ glasses are investigated. The optical absorption spectra were recorded at room temperature in the UV-visible region. From the absorption edge studies, the values of optical bandgap energies have been evaluated. The refractive index, molar refraction and polarizability of oxide ions have been calculated by using Lorentz–Lorentz relations. The non-linear variations of the above optical parameters are discussed with respect to samarium concentration.

Keywords. Optical bandgap; refractive index; tellurite glasses.

1. Introduction

Tellurite glasses are very promising materials for linear and non-linear application in optics, due to some of their important characteristic features such as high refractive index, low phonon maxima and low melting temperature (Vijaya Prakash *et al* 2001). TeO_2 is known as a conditional glass former, as it needs a modifier in order to form the glassy state easily (Halimah *et al* 2005). Tellurite glasses continue to intrigue both academic and industry researchers not only because of their technical applications, but also owing to a fundamental interest in understanding their microscopic mechanisms. In general, application and utilities of glassy materials are enormous and are governed by the factors like composition, refractive index and dopants present in the glasses.

Moreover, the rare earth in glassy matrix is strongly dependent on crystal field effects, local environment, phonon energies extended into the bandgap (Vijaya Prakash 2000). It has been found that glasses with a high density along with a low dispersion usually have a high non-linear refractive index. The heavy metal oxide glasses containing PbO , Bi_2O_3 and Ga_2O_3 are reported (Lapp *et al* 1989; Daumbaugh and Lapp 1992) to have a high density and refractive index and excellent non-linear properties. There is a major and growing interest in developing photonic and signal processing devices for communications and computing applications (Vogel 1989; Komatsu *et al* 1991). Optical glasses are considered promising candidates for such devices because they can be made to possess a rapid non-linear response to an optical signal. Optical transparency over a large wavelength

range, physical, chemical and thermal properties are suitable for practical applications (Huang *et al* 1994). The present work intends to study the optical properties of $\text{Sm}_2\text{O}_3\text{-PbO-TeO}_2$ glasses and to discuss the variations of optical properties with respect to a small concentration of Sm_2O_3 .

2. Materials and methods

Analar grade samarium trioxide (Sm_2O_3), lead oxide (PbO) and tellurium dioxide (TeO_2) were used as starting materials for preparation of glass samples. Different compositions of glasses were prepared by using conventional melt quenching method. The detailed experimental method was reported elsewhere (Eraiah 2006). The density of each glass was measured based on the Archimedes method using toluene as an immersion liquid (density = 0.860 g/cm^3 at RT). The corresponding molar volumes (V_m) are calculated by using the formula

$$V_m = M/\rho,$$

where M is the molecular weight and ρ the density of glass samples. The optical absorption of the polished samples was obtained in the wavelength range 200–800 nm at room temperature by using Hitachi-U-3200 absorption spectrometer. The optical absorption coefficient ($\alpha(\nu)$), was calculated for each sample by using the relation

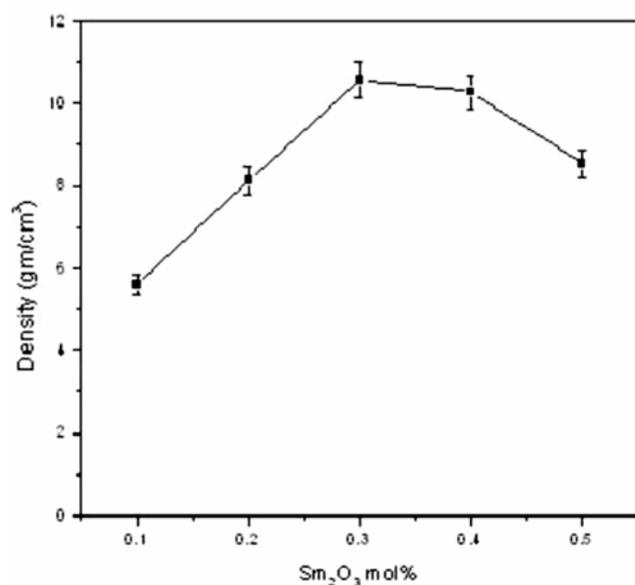
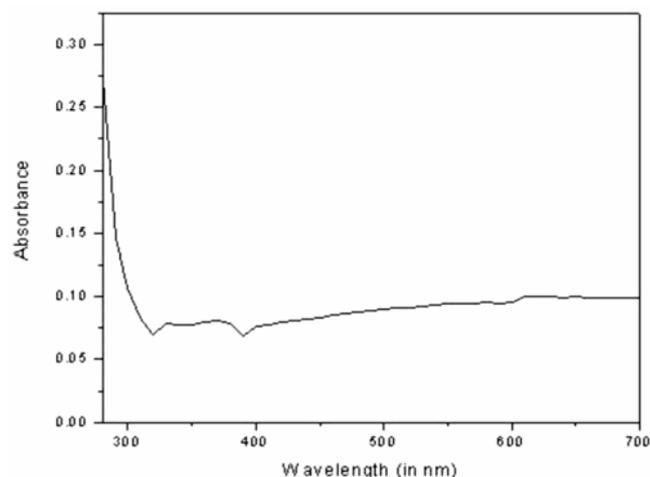
$$\alpha(\nu) = A/d,$$

where A is absorbance and d the thickness of the samples. Optical bandgap energies (E_g) are calculated by the extrapolation of the linear region to meet $h\nu$ axis at

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Table 1. Density, molar volume, optical energy bandgap, refractive index, molar refraction and polarizability of oxide ion for $\text{Sm}_2\text{O}_3\text{-PbO-TeO}_2$ glasses.

Glass composition (mol%)			Density (ρ) (g/cm ³)	Molar volume (V_m) (cm ³)	Energy bandgap (E_g) (eV)	Refractive index (n)	Molar refraction (R_M) (cm ³)	Polarizability (α_e) ($\times 10^{-24}$) (cm ³)
Sm_2O_3	PbO	TeO ₂						
0.0	40	60	5.6027	33.0200	2.8201	2.4409	20.6179	8.1713
0.1	39.9	60	5.6102	33.0044	3.6594	2.2444	18.9346	3.8354
0.2	39.8	60	8.1301	22.7902	3.6943	2.2318	12.9962	2.6294
0.3	39.7	60	10.5778	17.5284	3.9660	2.1764	9.7226	1.08266
0.4	39.6	60	10.2894	18.0319	3.6555	2.2399	10.3228	1.1151
0.5	39.5	60	8.5500	21.7150	4.5370	2.0735	11.3735	2.2682

**Figure 1.** Variation of density as a function of Sm_2O_3 .**Figure 2.** A typical absorption spectrum of $\text{Sm}_2\text{O}_3\text{-PbO-TeO}_2$ glasses.

$(\alpha h\nu)^{1/2} = 0$. Refractive indices of these glasses are calculated by using the relation,

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

which was proposed by Dimitrov and Sakka (1996).

The molar refraction (R_M) was calculated by using the relation

$$\frac{n^2 - 1}{n^2 + 2} \left(\frac{M}{\rho} \right) = R_M, \quad (2)$$

and the polarizabilities of these glasses have been estimated by using the Lorentz-Lorentz (Rawson 1980) relation

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

3. Results and discussion

The measured and calculated values of densities, molar volumes, energy bandgaps, refractive indices, molar refractions and polarizability of oxide ions of samarium doped lead-tellurite glasses are listed in table 1. The variation of density vs mol% of Sm_2O_3 is shown in figure 1. As can be seen from figure 1, the density increases up to 0.3 mol% and it starts to decrease from 0.4 mol%. This behaviour may be due to less number of non-bridging oxygen up to 0.3 mol% of Sm_2O_3 , then there is a creation of more number of non-bridging oxygen on increasing the mol% of Sm_2O_3 and again the density suddenly drops at 0.5 mol% of Sm_2O_3 . The variation of molar volume vs mol% of Sm_2O_3 is exactly opposite to that of density variation is expected. A typical absorption spectrum of $\text{Sm}_2\text{O}_3\text{-PbO-TeO}_2$ glasses is shown in figure 2. In amorphous materials the absorption due to the band-to-band transitions that determines the optical energy gap was interpreted by Mott and Davis (1970) and can be written in general form

$$\alpha(\nu) = (B/h\nu) (h\nu - E_{\text{opt}})^n, \quad (4)$$

where B is a constant and $h\nu$ the photon energy, E_{opt} the optical energy gap and n an index which can have any values between 1/2 and 3 depending on the nature of the

inter-band electronic transitions (Al-Ani and Higazy 1991). The goodness-of-fit of the data to the formula for either $n = 1/2$ (direct bandgap) or $n = 2$ (indirect bandgap) is determined. The absorption coefficients, $\alpha(\nu)$, are 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 fit well to (4) for $n = 2$. Therefore, the results are plotted as $(\alpha h\nu)^{1/2}$ vs photon energy ($h\nu$), a typical plot is shown in figure 3, 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 ($h\nu$). This suggests that at higher photon energies the transitions occurring in the present glass samples are of indirect type. The variation of optical energy bandgap

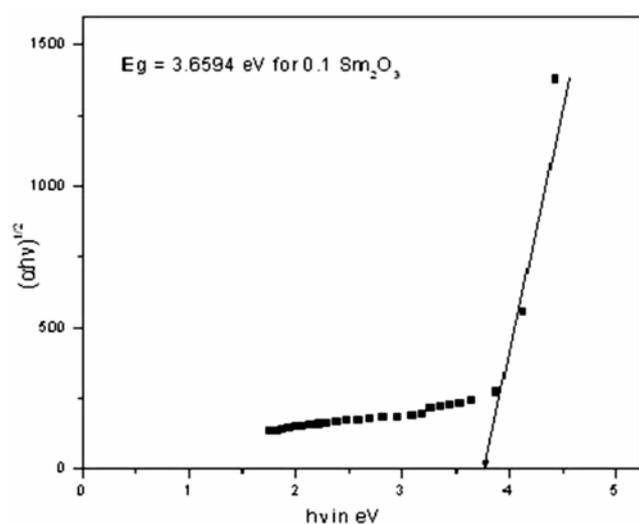


Figure 3. A typical plot of $(\alpha h\nu)^{1/2}$ vs photon energy ($h\nu$).

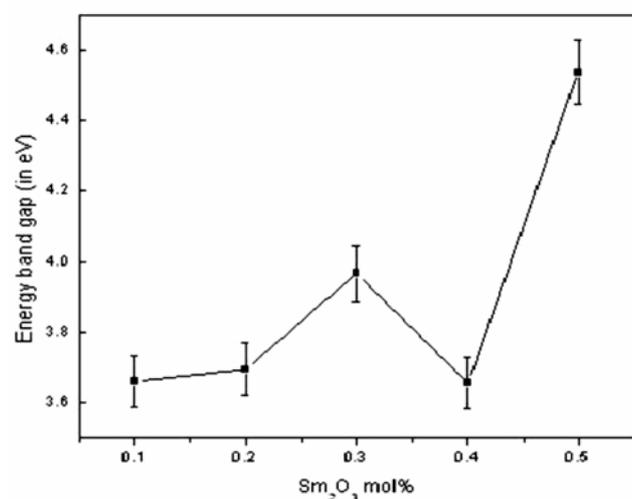


Figure 4. Variation of optical energy bandgap values vs mol% of Sm_2O_3 .

values vs mol% of Sm_2O_3 is shown in figure 4. The E_g values increase linearly with increase of Sm_2O_3 up to 0.3 mol% and suddenly drops at 0.4 mol% and again it increases at 0.5 mol% of Sm_2O_3 . This may be due to the creation of more non-bridging oxygen at 0.4 mol% of Sm_2O_3 and hence a glass structure change takes place. This also may be due to the presence of higher valence oxide ion, Pb^{2+} , when it is acting as a modifier, the cations present in the network can produce important structural effects. There are reports in the literature which suggest that Zn^{2+} , Mg^{2+} , Pb^{2+} etc occupy both network and non-network positions (Kim and Bray 1974; Ganguli and Rao 1999; Ganguli *et al* 1999). More probably, PbO ionizes as Pb^{2+} and O^{2-} and results in modifying the network. At 0.4 mol% Sm_2O_3 , part of Pb is likely to behave as a network former. Due to this reason energy bandgap variation takes place at 0.4 mol% of Sm_2O_3 . Figure 5 shows the variation of refractive indices vs mol% of Sm_2O_3 , the trend in variation is exactly opposite to the energy bandgap variation as expected. In these glasses the glass-forming network is formed by O–Pb–O linkages with $[\text{PbO}_6]$ octahedral and $[\text{PbO}_4]$ tetrahedral (Nachimuthu and Jagannathan 1995). The s and p orbitals of Pb^{2+} and p orbital of oxygen interact with each other to form bonding and antibonding states which give rise to valence bond and conduction bond, respectively. The number of strong O–Pb–O linkages increases resulting in the narrowing of the bandgap energies (Vithal *et al* 1997) which can account for the increase of refractive index at the composition, 0.4, as well as decrease for the compositions corresponding to 0.3 and 0.5 mol% of Sm_2O_3 . Figure 6 shows the variation of polarizability of oxide ions vs mol% of Sm_2O_3 . As can be seen from figure 6 the polarizability decreases gradually up to 0.3 mol% of Sm_2O_3 then increases suddenly from 0.4 mol% to 0.5 mol%

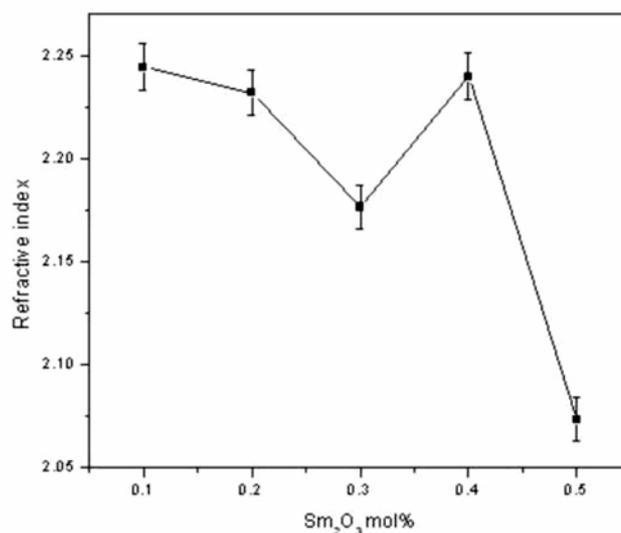


Figure 5. Variation of refractive indices vs mol% of Sm_2O_3 .

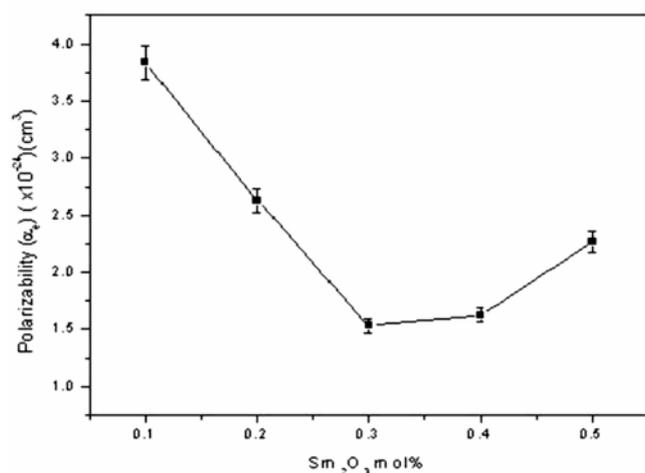


Figure 6. Variation of polarizability of oxide ions vs mol% of Sm₂O₃.

of Sm₂O₃. This may be due to breaking of Te–O–Te bonds when Pb enters into network position and formed new non-bridging bonds like Te–O–Pb²⁺. Also a substitution of cations into TeO₂ network induces a structural variation from (TeO₄)⁴⁻ to (TeO₃)²⁻ entities through an intermediate asymmetric structure (Neov *et al* 1979). This leads to a significant change in the optical properties.

4. Conclusions

Sm₂O₃–PbO–TeO₂ glasses have been prepared and their optical properties are investigated. Densities and energy bandgaps are discussed in terms of the glass composition and structure. In both the cases the variation with respect to samarium concentration is found to be similar at 0.4 mol% of Sm₂O₃. This variation is also reflected in

refractive indices and polarizability of oxide ions. In these glasses the variation at 0.4 mol% Sm₂O₃ was not only due to the presence of Sm²⁺ ions, but also due to the dual role of Pb²⁺ ions, which are responsible for significant change in the optical properties of these glasses.

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