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Optical properties of samarium doped zinc–tellurite glasses

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Abstract. Glasses with the composition, $(Sm_2O_3)_x(ZnO)_{(40-x)}(TeO_2)_{(60)}$, were prepared by conventional melt quenching method. The density, molar volume, and optical energy band gap of these glasses have been measured. The refractive index, molar refraction and polarizability of oxide ion have been calculated by using Lorentz–Lorentz relations. Optical absorption spectra of these glasses were recorded in the range 300–700 nm at room temperature. The oxide ion polarizabilities deduced from two different quantities, viz. refractive index and optical energy band gap, agree well compared with other glasses. The nonlinear variation of the above optical parameters with respect to samarium dopant has been explained.

Keywords. Glasses; density; refractive index; optical properties; tellurium oxide.

1. Introduction

Tellurium oxide (TeO_2) based glasses are of scientific and technological interest on account of their unique properties such as chemical durability, electrical conductivity, transmission capability, high dielectric constant, high refractive indices and low melting points (Nasu *et al* 1990; Tanaba *et al* 1990). The application of tellurite glasses in industries (Stanworth 1952; Burger *et al* 1985) such as electric, optical, electronic and other fields are immense due to their good semiconducting properties. Tellurite glasses have recently gained wide attention because of their potential as hosts of rare earth elements for the development of fibres and lasers covering all the main telecommunication bands (Nunziconti *et al* 2004), and promising materials for optical switching devices (Sidkey and Gaafar 2004). Recently, tellurite glasses doped with heavy metal oxides or rare earth oxides (El-Mallawany *et al* 1995; El-Mallawany 1998; Berthereau *et al* 1996) such as Nb_2O_3, CeO_2 or ZnO have received great scientific interest because these oxides can change the optical and physical properties of the tellurite glasses.

One of the most important concerns in rare earth doped glasses is to define the dopant environment. Hypersensitive transitions are observed in the spectra of all rare earth ions having more than one *f* electron (Tikhomirov *et al* 1999). Hypersensitive transitions of rare earth ions manifest as anomalous sensitivity of line strength to the character of the dopant environment (Misra and Sommerer 1991).

Optical absorption in solids occurs by various mechanisms, in all of which the photon energy will be absorbed by either the lattice or by electrons where the transferred energy is covered. The lattice (or phonon) absorption will give information about atomic vibrations involved and this absorption of radiation normally occurs in the infrared region of the spectrum. Optical absorption is a useful method for investigating optically induced transitions and for getting information about the band structure and energy gap of non-crystalline materials. The principle of this technique is that a photon with energy greater than the band gap energy will be absorbed (Abd El-Ati and Higazy 2000; Kumar *et al* 2000).

Refractive index is one of the most important properties in optical glasses. Therefore, a large number of researchers have carried out investigations to ascertain the relation between refractive index and glass composition. It is generally recognized that the refractive index, n, and density, r, of many common glasses can be varied by changing the base glass composition (El-Mallawany 1992).

The polarizability is one of the most important properties that govern the non-linearity response of the material. The optical non-linearity is caused by electronic polarization of the materials upon exposure to intense light beams. Polarizability is related to many macro and microscopic physical and chemical properties such as optical UV absorption of metal ions, electro-optical effect etc (Dimitrov and Sakka 1996). Among the theoretical expressions, the Lorentz–Lorentz equation (Rawson 1980) relates the polarizability, a_e, to the refractive index, n, as follows

$$\frac{n^2-1}{n^2+2}(V_m) = 4/3p\,Na_e, \tag{1}$$

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where V_m is the molar volume, N the Avogadro number, α_e the polarizability; when (1) is expressed in terms of the specific mass or density, ρ, it reduces to

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

and describes the specific refraction, R, to the material. The molar refraction, R_M, is

$$\frac{n^2-1}{n^2+2}\left(\frac{M}{\rho}\right)=R_M, \tag{3}$$

where M is the molecular weight of the material and M/ρ the molar volume. Equations (2) and (3) are the well known Lorentz–Lorentz equations. R_M and n depend on the polarizability of the material.

2. Experimental

2.1 *Sample preparation*

The glasses having composition, $(Sm_2O_3)_x(ZnO)_{(40-x)}(TeO_2)_{(60)}$ (where x = 0·1–0·5 mol%), were prepared by using conventional melt quenching method. The mixtures of Analar grade tellurium dioxide (TeO_2), zinc oxide (ZnO) and samarium trioxide (Sm_2O_3) chemicals were used as starting materials. The detailed experimental procedure was explained elsewhere (Eraiah and Anavekar 2001). All the samples were annealed at 200°C for 1 h to eliminate thermal and mechanical stresses. The amorphous nature of these glasses was examined by X-ray diffraction analysis at room temperature using CuKα radiation. The diffraction pattern did not show any sharp peaks, confirming the amorphous nature of the samples.

2.2 *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/cm^3 at room temperature). The corresponding molar volumes (V_m) were calculated by using the relation, $V_m = M/\rho$, where M is the molecular weight and ρ the corresponding glass samples.

2.3 *Optical absorption and energy band gap*

The optical absorption was conducted on polished glass samples; the optical absorption spectra of these glass samples were recorded using Hitachi-U-3200 absorption spectrophotometer in the wavelength region 300–700 nm at nominal incidence. The optical absorption coefficient, $\alpha(n)$, was calculated for each sample at different photon energies by using the relation, $\alpha(n) = A/d$, where A is the absorbance and d the thickness of the samples. Optical energy band gap (E_g) was calculated by the interpolation of the linear region to meet $h\nu$ axis at $(\alpha h\nu)^{1/2} = 0$ (α = absorption coefficient).

2.4 *Refractive index, molar refraction and polarizability*

Refractive index of samarium doped zinc–tellurite glasses was calculated by using the relation

$$\frac{n^2-1}{n^2+2}=1-\sqrt{Eg/20}, \tag{4}$$

which was proposed by Dimitrov and Sakka (1996). The molar refraction (R_M) was calculated by using the relation (3) and the polarizability of these glasses has been estimated by using the relation (2).

3. Results and discussion

The measured and calculated values of densities, molar volumes, optical energy band gaps, refractive indices, molar refractions and polarizability of oxide ions for samarium doped zinc–tellurite glasses are listed in table 1.

3.1 *Density and molar volume*

Density is an effective tool to explore the degree of structural compactness (Rami Reddy *et al* 1995) modification of the geometrical configurations of the glass network, change in coordination and the variation of dimensions of the interstitial holes. Figure 1 shows the variation of density vs mol% of Sm_2O_3. Density increases up to 0·4 mol% of Sm_2O_3, then it suddenly drops at 0·5 mol% of Sm_2O_3. This indicates that by addition of small amount of Sm_2O_3 into ZnO–TeO_2 glass network, initially it may resist the creation of non-bridging oxygens hence the density increases. With further increase in Sm_2O_3 concentration, the creation of non-bridging oxygens takes place, and then the density suddenly drops at 0·5 mol% of Sm_2O_3. The behaviour of molar volume mainly depends upon the density of glasses, hence the variation of molar volumes in these glasses are as expected.

3.2 *Optical absorption and energy band gap (E_g)*

Figure 2 shows the typical absorption spectrum of samarium doped zinc–tellurite glasses. The absorption coefficient, $\alpha(n)$, was determined near the absorption edge, at different photon energies for all investigated glass samples. The quantity, $\alpha(n)$, can be displayed in a number of ways as described by the relation

Table 1. Density, molar volume, optical energy band gap, refractive index, molar refraction and polarizability of oxide ion for Sm_2O_3–ZnO–TeO_2 glasses.

Glass composition (mol%)			Density (r)	Molar volume	Energy band gap	Refractive	Molar refraction	Polarizability (a_e)
Sm_2O_3	ZnO	TeO_2	(g/cm^3)	(V_m) (cm^{-3})	(E_g) (eV)	index (n)	(R_M) (cm^3)	($\times 10^{-24}$) (cm^3)
0	40	60	10·645	12·33	3·000	2·397	7·554	2·994
0·1	39·9	60	5·846	22·33	3·093	2·372	13·547	5·370
0·2	39·8	60	7·464	17·52	3·199	2·345	10·512	4·167
0·3	39·7	60	11·373	11·52	3·344	2·309	6·808	2·699
0·4	39·6	60	13·872	9·47	3·379	2·301	5·576	2·210
0·5	39·5	60	7·393	17·80	2·220	2·646	11·869	4·705

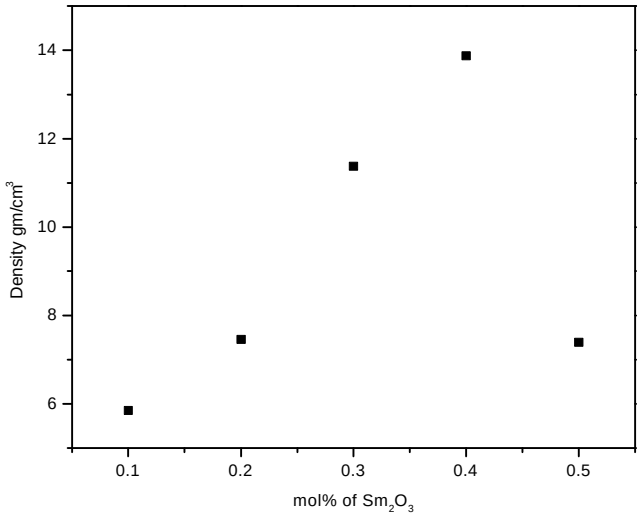

Figure 1. Variation of density vs Sm_2O_3 in Sm_2O_3–ZnO–TeO_2 glasses.

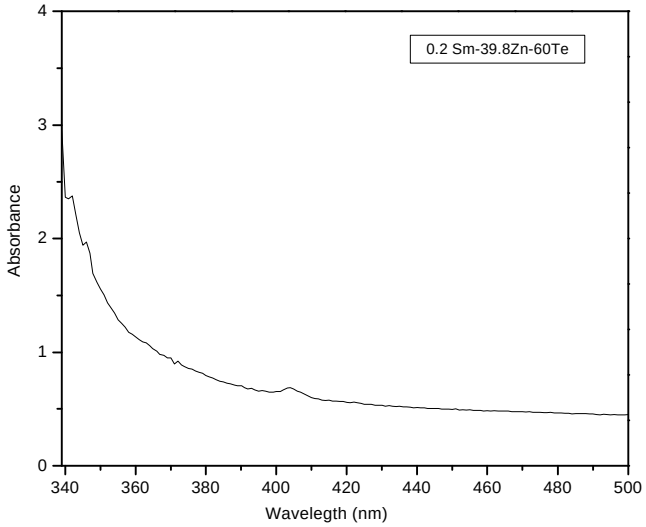

Figure 2. Optical absorption spectrum in Sm_2O_3–ZnO–TeO_2 glasses.

$$a(n) = B(hn - E_g)^n/hn, \quad (5)$$

where B is a constant, E_g the optical band gap energy and the index, n, can have any value between 0·5 and 3 depending on the nature of the inter-band electronic transitions (Al-Ani and Higazy 1991). It has been observed that for indirect allowed transitions the measured absorption fits well to the above (5) for $n = 2$. These results are, therefore, plotted as $(ahn)^{1/2}$ vs photon energy (hn) in figure 3, for indirect allowed transitions to find the values of the optical band gap (E_g). The variation of optical energy band gap (E_g) values vs mol% of Sm_2O_3 is as shown in figure 4. The E_g increases linearly with increase of Sm_2O_3 concentration up to 0·4 mol% and then drops suddenly at 0·5 mol% of Sm_2O_3. The sudden drop of E_g may be due to the variation of density as well as the variation of non-bridging oxygens. Another reason could be that at high dopant concentrations, the broadening of the impurity band and the formation of band tails on the edges of the conduction and valence bands would lead to a reduction in E_g as in semiconductors (Aw *et al* 1991).

3.3 *Refractive index (n), molar refraction (R_M) and polarizability (a_e)*

Refractive index (n) depends upon the composition of an optical material. Molar refraction (R_M) and n depend on the polarizability of the material. The more polarizable the outer electrons, the higher the refractive index and also higher the molar refraction. As can be seen from table 1 refractive index decreases with increasing concentration of Sm_2O_3 up to 0·4 mol% then the value of n suddenly increases at 0·5 mol% of Sm_2O_3; the same trend has been observed in the case of molar refraction. Also, polarizability decreases with the increase of concentration of Sm_2O_3 up to 0·4 mol%, then it decreases at 0·5 mol% of Sm_2O_3, however, the value compared to 0·4 mol% is higher. The variation of these three parameters can be explained as follows.

Knowing the chemical composition of the glass and its density, the number of atoms per unit volume (N/V) can be calculated which mainly depends on the modifier content. However, these changes are not sufficient to account for

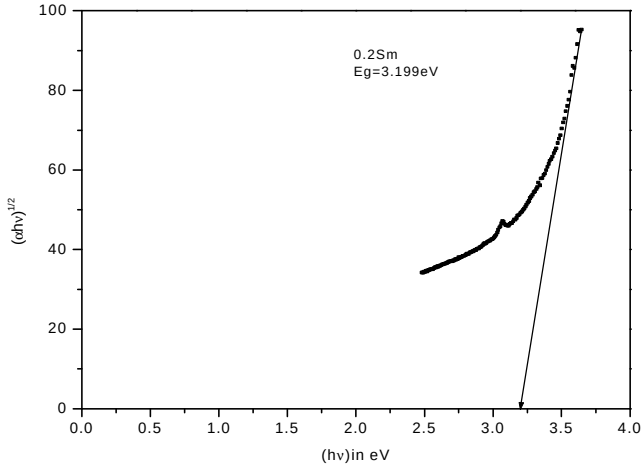

Figure 3. Variation of $(ahn)^{1/2}$ vs (hn) in Sm_2O_3–ZnO–TeO_2 glasses.

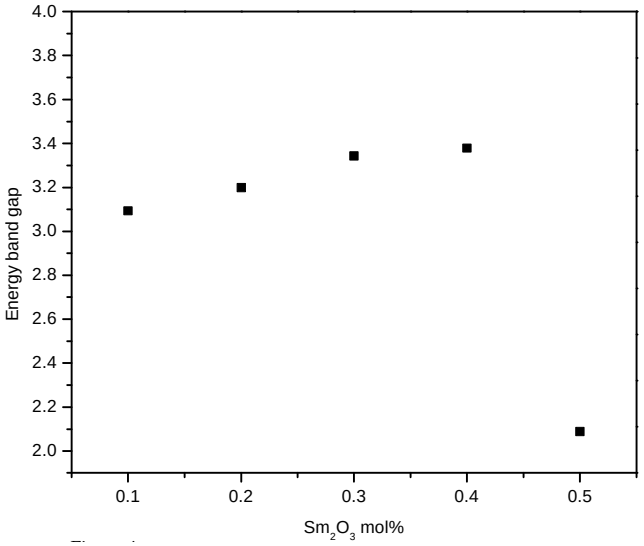

Figure 4. Variation of energy band gap vs Sm_2O_3 in Sm_2O_3–ZnO–TeO_2 glasses.

the observed decrease in the refractive index. With the substitution of ZnO oxides into TeO_2, bridging Te–O–Te bonds are broken and non-bridging Te–O–Zn^{2+} bonds are formed. The non-bridging oxygen (NBO) bonds have a much greater ionic character and much lower bond energies. Consequently, the NBO bonds have higher polarizability and cation refractions. The variation of n and a_e at 0·4 mol% Sm_2O_3 may be also due to the dual nature of ZnO, it acts as network modifier up to 0·4 mol% then it may occupy the network former position (Ganguli *et al* 1999).

4. Conclusions

Samarium doped zinc–tellurite glasses were prepared by melt quenching method and the amorphous nature of these glasses was studied by X-ray diffraction. Density and optical band gap of these glasses increases up to 0·4 mol% of Sm_2O_3 due to addition of modifier oxide which breaks up the Te–O–Te linkage and creates non-bridging oxygens. However, at 0·5 mol% Sm_2O_3 the density and energy band gap suddenly drops due to change in position of Zn^{2+} ion in the glass network as glass former and hence there is structural change in glass network. While in the case of molar volume, refractive index and polarizability of oxide ions decrease with respect to Sm_2O_3 concentration up to 0·4 mol% and then increases at 0·5 mol% of Sm_2O_3 concentration as expected. This indicates that rare earth oxide doped telluride based glasses have quite different electronic structure.

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