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Optical properties of samarium doped zinc–phosphate glasses

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Abstract

Samarium doped zinc–phosphate glasses having composition Sm_2O_3 $_{(x)}ZnO_{(60-x)}$ P_2O_5 $_{(40)}$ (where $x = 0.1$–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 3.34 to 3.87 gm/cm^3 and those of molar volume range from 27.62 to 31.80 cm^{-3}. The optical absorbance studies were carried out on these glasses to measure their energy band gaps. The absorption spectra of these glasses were recorded in UV-visible region. No sharp edges were found in the optical spectra, which verifies the amorphous nature of these glasses. The optical band gap energies for these glasses were found to be in the range of 2.89–4.20 eV. The refractive index and polarizability of oxide ion have been calculated by using Lorentz–Lorentz relations. The values of refractive index range from 2.13 to 2.42 and those of polarizability of oxide ion range from 6.51×10^{-24} to 7.80×10^{-24} cm^3.

Keywords: A. Glasses; D. Optical properties

1. Introduction

Interest in the study of phosphate glasses arose due to their easy preparation and low melting points compared with borate and silicate glasses, which have been studied extensively. Recently, phosphate glasses have received a great deal of attention due to their considerable applications in optical data transmission, detection, sensing and laser technologies [1]. Rare earth doped glasses in recent years have been studied because of their applications as active media for the fiber lasers, optical amplifiers, etc. [2,3]. One of the most important concerns in rare earth doped glasses is to define the dopant environment [4].

The study of optical absorption spectra in solids provides essential information about the band structure and the energy gap in the crystalline and non-crystalline materials. The principle of this technique is that a photon with energy greater than the band gap energy will be absorbed. Analysis of the absorption spectra in the lower energy part gives information about the atomic vibrations, while the higher energy part of spectrum gives knowledge about the electronic state in the atoms [1]. Measurement of the optical absorption coefficient near the fundamental absorption edge is a standard method for the investigation of optically induced electronic transitions in many materials. When an electromagnetic wave interacts with a valence electron both direct and indirect optical transitions occur across the energy gap. However, indirect transitions involve simultaneous interaction with lattice vibrations and the wave vector of the electron [5].

Refractive index is one of the 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 [6].

The polarizability is also 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. [7].

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2. Theory

The absorption coefficient, $\alpha(v)$ in amorphous materials, in the optical region near the absorption edge at particular temperature, obeys empirical relation known as, Urbach rule [8] given by

$$\alpha(v) = \alpha_0 \exp(hv/E_c), \tag{1}$$

where hv is photon energy, α_0 is a constant and E_c is an energy which interpreted as the width of the localized state in the normally forbidden band gap which is also known as the Urbach energy.

Optical absorption in solids and liquids occur by various mechanisms in all of which the photon energy will be absorbed by either lattice or by electrons where the transferred energy is conserved. The lattice (or phonon) absorption will give information about the atomic vibration involved and this absorption of radiation normally occurs in the infrared region of the spectrum. The higher energy parts of the spectrum particularly those associated with the interband electronic transition will provide further information about the electron states. In these processes, the electrons are excited from a filled band to an empty band by the photon absorption and as a consequence of this, a marked increase in the absorption coefficient $\alpha(v)$ will result. The onset of this rapid change in $\alpha(v)$ is called the 'fundamental absorption edge' and the corresponding energy is defined as the 'energy gap' [9].

In amorphous materials the absorption due to the band-to-band transitions that determines the optical energy gap was interpreted by Davis and Mott [10] and can be written in general form:

$$\alpha(v) = (B/hv)(hv\text{-}E_{opt})^n, \tag{2}$$

where B is a constant and hv the photon energy, E_{opt} the optical energy gap and n is an index which can have any values between $\frac{1}{2}$ and three depending on the nature of the interband electronic transitions [11]. The goodness of the fit of the data to the formula for either $n = \frac{1}{2}$ (direct band gap) or $n = 2$ (indirect band gap) is determined. It has been found that [10–14] for many amorphous materials, a reasonable fit of Eq. (2) with $n = 2$ are achieved. This is the case of indirect transitions, where the interactions with lattice vibrations take place.

Among the theoretical expressions, the Lorentz–Lorentz equation [15] relates the polarizability, (α_m), to the refractive index, (n), as follows

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

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

3. Experimental

3.1. Sample preparation

The glass samples having composition Sm_2O_3 $_{(x)}$ ZnO $_{(60-x)}$ P_2O_5 $_{(40)}$ (where $x = 0.1$–0.5 mol%) were prepared by melt quenching method. The mixtures of analytical grade ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$), zinc oxide (ZnO) and samarium trioxide (Sm_2O_3) used as staring materials. The detailed experimental procedure was explained elsewhere [16]. The samples were annealed at 200 °C for two hours to eliminate mechanical and thermal stresses. The amorphous nature of these glasses was examined by X-ray diffraction analysis at room temperature. The X-ray diffraction spectra of all samples showed the diffused bands characteristic of the 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/cm^3). The corresponding molar volumes were calculated by using the relation $V_m = M/\rho$, where M is 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 $\alpha(v)$ was calculated for each sample at different photon energies by using the relation $\alpha(v) = A/d$, 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

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

which was proposed by Dimitrov et al. [7]. The polarizability of oxide ions for these glasses was estimated by using the relation (3).

4. Results and discussion

The measured and calculated values of densities, molar volumes, optical energy band gaps, refractive indices and polarizability of oxide ions for Sm_2O_3–ZnO–P_2O_5 glasses are listed in Table 1. The measured densities of these glasses are depicted in Fig. 1. As can be seen from the figure

Table 1
Density, molar volume, energy band gap, refractive index and polarizability of oxide ions of Sm_2O_3–ZnO–P_2O_5 glasses

Glass composition			Density (ρ) (gm/cm^3)	Molar volume (V_m) (cm^3)	Optical band gap (E_{opt}) (eV)	Refractive index (n)	Polarizability of oxide ions (α_m) $\times 10^{-24}$ cm^3
Sm_2O_3 (mol%)	ZnO (mol%)	P_2O_5 (mol%)					
0.1	59.9	40	3.485	30.38	4.208	2.13	6.519
0.2	59.8	40	3.386	31.34	3.753	2.219	7.042
0.3	59.7	40	3.346	31.8	2.898	2.425	7.808
0.4	59.6	40	3.482	30.63	2.958	2.408	7.473
0.5	59.5	40	3.871	27.62	2.984	2.401	6.709

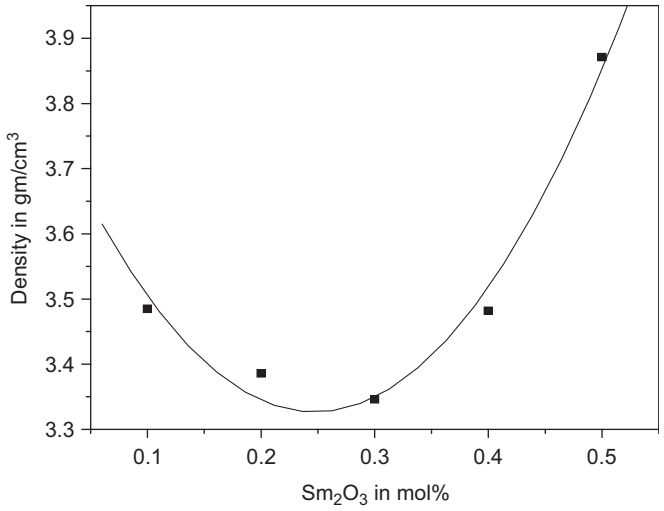

Fig. 1. Variation of density versus Sm_2O_3 mol%.

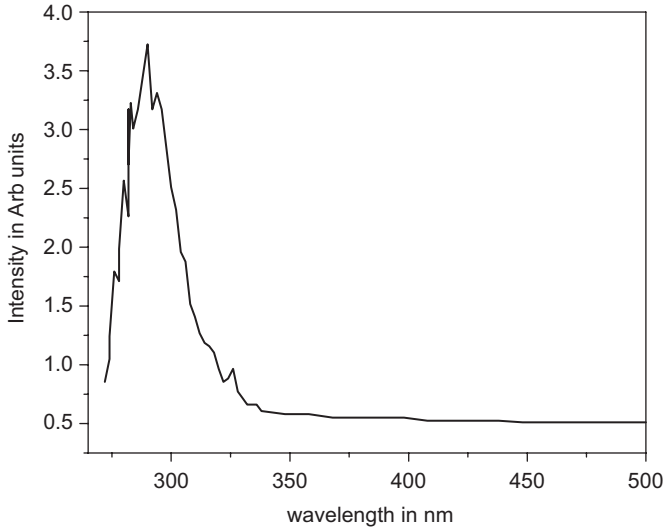

Fig. 2. A typical absorption spectrum of Sm_2O_3–ZnO–P_2O_5 glass system.

that, by the addition of Sm_2O_3 into the ZnO–P_2O_5 glass network, the density decreases up to 0.3 mol% of Sm_2O_3. Further addition of Sm_2O_3 (0.4 mol%) results in the increase of density. This indicates that by addition of Sm_2O_3 into the glass network, the non-bridging oxygen increases so that density decreases up to 0.3 mol% of Sm_2O_3. It can also be observed that density decreases with decreasing concentration of ZnO, which act as an intermediate/modifier in glass system. Addition of ZnO in phosphate glasses shows an increase in oxygen packing density, which squeezes the structure of the sample [5]. At 0.4 mol% Sm_2O_3, due to increase in oxygen packing density the structure becomes more compact and hence the density increases, the molar volume also increase up to 0.3 mol% and then decreases as expected is shown in Table 1.

Fig. 2 shows the typical absorption spectrum of samarium doped zinc–phosphate glasses. The absorption coefficients, $\alpha(v)$, 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 to Eq. (2) for $n = 2$. Therefore, the results were plotted as $(\alpha hv)^{1/2}$ versus photon energy (hv) a typical plot is shown in Fig. 3, for indirect

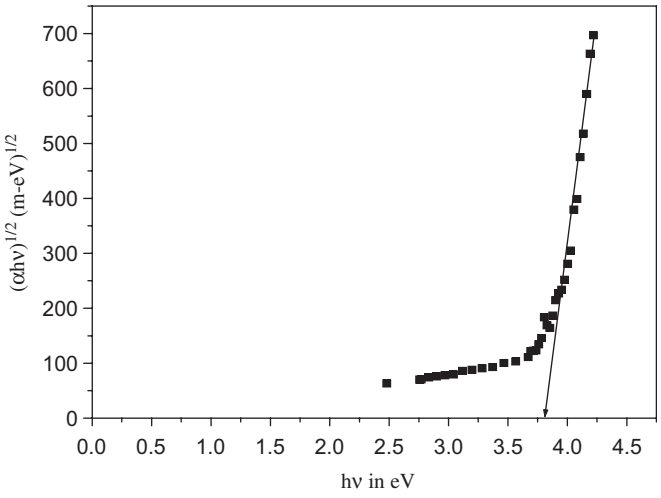

Fig. 3. A typical plot of $(\alpha hv)^{1/2}$ versus (hv) in Sm_2O_3–ZnO–P_2O_5 glasses.

allowed transitions to find the values of optical band gap, E_{opt}. It can be seen that there exists a linear dependence of $(\alpha hv)^{1/2}$ in the photon energy (hv). This suggests that at higher photon energies the transitions occurring in the

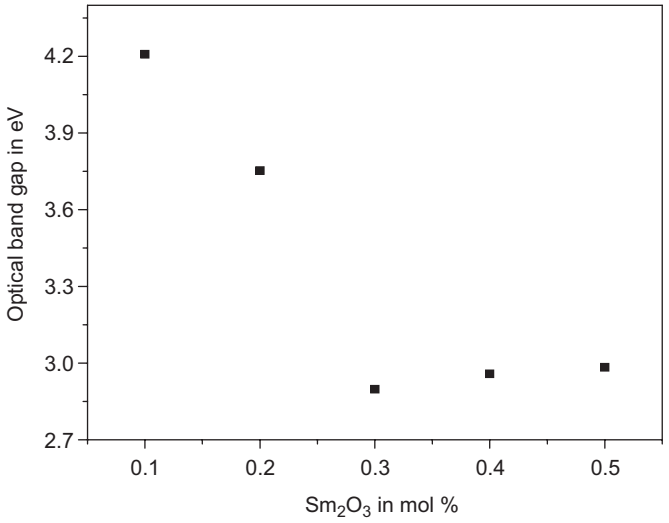

Fig. 4. Variation of optical band gap versus Sm_2O_3 mol%.

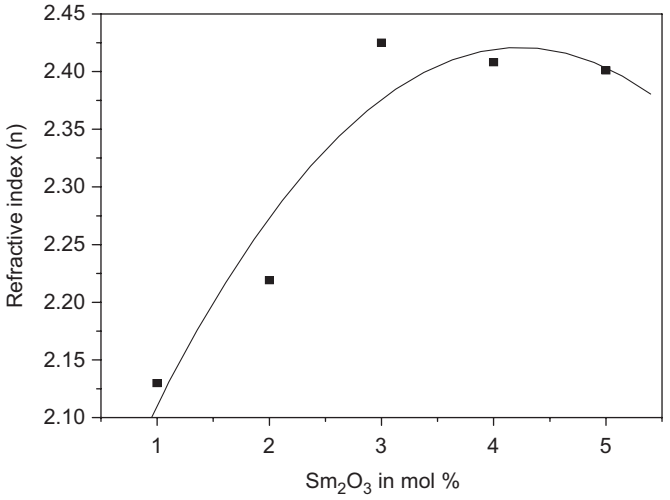

Fig. 5. Variation of refractive index versus Sm_2O_3 mol%.

present glass samples are of indirect type. The values of the optical band gaps obtained are listed in Table 1 and are depicted in Fig. 4 as a function of Sm_2O_3. It can be noticed that the optical band gap decreases with increase of Sm_2O_3 concentration up to 0.3 mol%. Further addition of Sm_2O_3 results in the slight increase in the optical band gap. This trend of results is similar to the behavior of density of these glasses.

Depolymerization is known to occur in phosphate glasses with the addition of alkali oxides, alkaline earth oxides and many other divalent metal oxides such as ZnO, PbO, etc. [17], consequently the average chain length is shortened. It also opens up the chain by breaking those oxygen bonds, which form a bridge between the corners of PO_4 tetrahedra. In this way, amount of non-bridging oxygen grows to high concentration due to a change in the oxygen bonding. It is generally accepted that absorption edge depends on the oxygen bond strength in the glass-forming network [18]. This process changes the oxygen bonding in glass forming network and any change of oxygen bonding in glass network such as the formation of non-bridging oxygen changes the absorption characteristics. This explains why the optical band gap decreases with increasing Sm_2O_3 up to 0.3 mol% and increases beyond 0.3 mol% of Sm_2O_3. The change in structure of glass may takes place at 0.4 mol% of Sm_2O_3 due to dual nature of ZnO. It acts as network modifier up to 0.4 mol% of Sm_2O_3 and then it may occupy the network former position [19].

Fig. 5 shows the variation of refractive index versus mol% of Sm_2O_3. As can be seen from the figure refractive index increases gradually with increasing the concentration of Sm_2O_3 up to 0.3 mol% then the value slowly decreases at 0.4 mol% of Sm_2O_3. Fig. 6 shows the variation of polarizability of oxide ions versus mol% of Sm_2O_3. Polarizability also increases initially up to 0.3 mol% then it starts decreases at 0.4 mol% of Sm_2O_3. This indicates that an addition of Sm_2O_3 content into $ZnO–P_2O_5$ glass

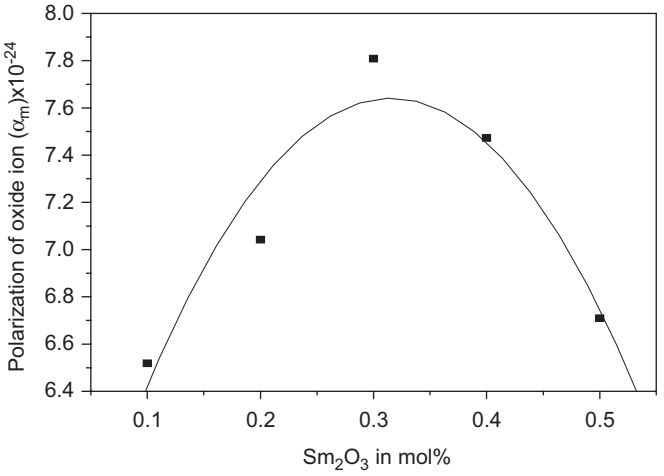

Fig. 6. Variation of polarizability of oxide ions versus Sm_2O_3 mol%.

network breaks up the PO_4 tetrahedral bonds creates non-bridging oxygen atoms at 0.3 mol% of Sm_2O_3. Therefore, the decreasing trend has been observed both in refractive index and polarization of oxide ions at 0.4 mol% of Sm_2O_3.

5. Conclusions

The measured density decreases with increasing concentration of Sm_2O_3 and molar volume increases up to 0.3 mol% of Sm_2O_3. Further increase in the concentration of Sm_2O_3 density increases as well as molar volume decreases. The optical absorption data indicated that the values of E_{opt} were obtained for $n = 2$, i.e. indirect transitions take place. The trend of optical band gap results is similar to the behavior of density of these glasses. It is concluded that amount of non-bridging oxygen grows due to a change in the oxygen bonding. The absorption

edge depends on the oxygen bond strength in the glass-forming network. However, by doping with Sm_2O_3 the optical band gap is constituted by the host materials ZnO and P_2O_5 does not alter much the band gap picture of the host glass. Hence very slight variation in the values of energy band gap, refractive index and polarization of oxide ions has been observed in the present glass system.

References

[1] M.I. Abd El-Ati, A.A. Higazy, J. Mater. Sci. 35 (2000) 6175.
[2] V. Aruna, N.V.V. Prasad, S. Buddhudu, Phys. Chem. Glasses 43 (12) (2002) 313.
[3] M. Tsuda, S. Soga, H. Inoue, A.N. Makishima, J. Appl. Phys. 85 (1999) 29.
[4] V.K. Tikhomirov, M. Naftaly, A. Jha, J. Appl. Phys. 86 (1) (1999) 351.
[5] M. Altaf, M. Ashraf Chaudhry, M. Zahid, J. Res. (Sci.) 14 (2) (2003) 253.
[6] R. El-Mallawany, J. Appl. Phys. 72 (5) (1992) 1774.
[7] V. Dimitrov, S. Sakka, J. Appl. Phys. 79 (3) (1996) 1736.
[8] F. Urbach, Phys. Rev. 92 (1953) 1324.
[9] C.A. Hogarth, A.A. Hosseini, J. Mater. Sci. 18 (1983) 2697.
[10] N.F. Mott, E.A. Davis, Philos. Mag. 28 (1970) 903.
[11] S.K.J. Al-Ani, A.A. Higazy, J. Mater. Sci. 26 (1991) 3670.
[12] A.A. Higazy, M.A. Hussein, M. Ewaida, M. Elhoft, J. Mater. Sci. Lett. 7 (1988) 453.
[13] A.A. Higazy, M.A. Hussein, M. Ewaida, J. Mater. Sci. Lett. 24 (1989) 2203.
[14] A.A. Higazy, B.Y. El-Baradic, M.I. Abd El-Ati, J. Mater. Sci. Lett. 11 (1992) 581.
[15] H. Rawson, Properties and Applications of Glasses, Elsevier, Amsterdam, 1980.
[16] B. Eraiah, R.V. Anavekar, Phys. Chem. Glasses 42 (1) (2001) 121.
[17] S. Chakraborty, A. Paul, J. Mater. Sci. Lett. 8 (1989) 1358.
[18] B.D. Mcswain, N.F. Borrel, S.V. Gongjen, Phys. Chem. Glasses 4 (1963) 1.
[19] M. Ganguli, M. Harishbhat, K.L. Rao, Phys. Chem. Glasses 40 (1999) 297.