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Spectroscopic Properties of Rare Earth Ion Doped TeO_2-B_2O_3-PbO Glass

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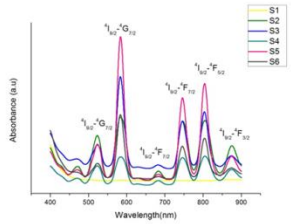
Graphical abstract



Abstract

This work focuses on the spectroscopic study of RE^{3+} ion, namely, trivalent neodymium (Nd^{3+}) doped lead borotellurite glass with a composition of TeO_2-B_2O_3-PbO. The glass sample has been prepared by conventional melt-quenching technique. 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. The absorption spectra are recorded using UV-Vis-NIR spectrometer in the range of 200-900 nm.

Keywords: Borotellurite glass; melt quenching; polarizability; refractive index; UV-Vis-NIR

1.0 INTRODUCTION

The interesting facts about the glass are its ability to acquire many unique properties such as high hardness, transparent and excellent corrosion resistance. Recently, lanthanide-doped glasses or in particular, Nd^{3+} ion doped tellurite glasses has attracted much interest due to their potential applications in many optical devices such as upconversion lasers, sensors, telecommunications, display devices, biological labeling and solar near infrared concentration for photovoltaic exploitation [1].

Due to some of their important characteristics and features, such as high refractive index, low loss phonon energy and low melting point, tellurite glasses are viewed as very promising materials for laser and non-linear applications in optics [2]. It is known as a conditional glass former that needs modifier ions to easily form the glassy state. The role of modifier oxides in the vitreous transition of tellurite melts is extremely important unlike traditional glass former such as P_2O_5, SiO_2 and B_2O_3 [3].

In upconversion (UC) phenomenon, two or more low energy excitation (absorbed) photons turn out in one higher energy (emitted) photon. Different materials have different ranges for UC emission. Rare earth materials show upconversion from near infra-red to UV/visible range. These materials can be used for various applications as upconversion phosphors, fluorescent labels, infrared detectors and 3D display. Different combinations of optically active rare earth materials can serve the purpose of upconversion in required range for a special application. A suitable host material is another necessity for good crystallization as well as UC emission. Oxides glass has shown excellent physical and chemical stability and hence, they are quite suitable to work as host matrix [4].

The electronic polarizability is one of the most important parameters for the application of glasses as optical and electronic materials. The non-linear response to the incident light exhibited by glassy materials is a function of electronic polarizability of the constituents in the glass matrix. The ability of glass formation, glass forming region, stability, chemical durability of the glass forming oxide materials like B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_3 etc, can be enhanced by adding metal oxides such as ZnO, TeO_2, PbO, Bi_2O_3 which are called conditional glass modifiers [5]. The following equations relate to the polarizability α_e, to the 'n';

$$[(n^2-1)/(n^2+2)]\, V_m = 4/3\pi N\alpha_e \quad (1)$$

where V_m is 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:

$$[(n^2-1)/(n^2+2)]\, M/\rho = R \quad (2)$$

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

$$[(n^2-1)/(n^2+2)]\, M/\rho = R_M \quad (3)$$

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.

The objective of this paper is to report on density, molar volume, optical band gap, refractive index, molar refraction and electronic polarizability of TeO_2-B_2O_3-PbO glasses.

2.0 EXPERIMENTAL

2.1 Sample Preparation

Glasses with composition: $80TeO_2$-$(10-x)B_2O_3$-$10PbO$-xNd_2O_3 (x=0, 0.5, 1.0, 1.5, 2.0, 2.5 mol%) were prepared from high purity raw materials. Appropriate amount of analytical agents were weighted and mixed thoroughly to obtain 10 g of mixed-powder. The mixture was melted in an alumina crucible inside a preheated electric furnace at 1000°C for between 10 and 15 min. The melt was then poured into a stainless steel mold and annealed for 5 h at 400°C to remove the mechanical and thermal stress. Finally the transparent glasses are cooled to room temperature. Samples are being allowed to cool down slowly to room temperature in the furnace. The samples of each composition were prepared and well-polished to perform detailed spectroscopic studies.

2.2 Density and Molar Volume

The density was measured at room temperature by Archimedes method, involving weighing in air and distilled water as the buoyancy liquid. All measurements were repeated 3 times and the average density were recorded. The accuracy of the results in duplicate measurements is 0.001 g/cm3. The molar volume was obtained through calculation. The corresponding molar volumes (V_m) were calculated by using relations $V_m = M/\rho$, where M is the molecular weight and ρ, the density of the corresponding glass samples.

2.3 Optical Absorption and Energy Band Gap

The absorption spectra of Nd^{3+} doped tellurite glasses were recorded in the range of 400-900 nm intervals using Shimadzu 3101 UV-VIS NIR scanning spectrophotometer. 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 absorbance and 'd' is 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 $(\alpha h\nu)^{1/2} = 0$.

2.4 RI, Molar Refraction and Polarizability

Refractive index of the glass samples were calculated using the following relation as proposed by Dimitrov and Sakka [5]:

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

The molar refraction (R_M) was calculated using the relation (3) and polarizability of these glasses has been estimated by using the relation (2). The polarizabilities are calculated on the basis of two different quantities namely the optical energy band gap for indirect transition and the refractive index [6].

3.0 RESULTS AND DISCUSSION

3.1 Density and Molar Volume

Table 1 shows the variation of densities vs mol % of Nd_2O_3. The density shows increment trend up to 2.0 mol % from 5.119 gcm^{-3} to 5.149 gcm^{-3}. Then, it suddenly drops at 2.5 mol % of Nd_2O_3. It might be due to the molecular weight of Nd (144.24 g/mol) is higher than the B (10.81 g/mol). These result would suggested that some structural rearrangement has occurred as the Nd_2O_3 content is increased.

Meanwhile, increment in density has a strong relation to the variation in molar volume. An addition of Nd (atomic radii~2.06) can replace B (atomic radii~0.87) with increase the free volume of the glass networking [7]. The molar volume is found to decrease from 30.93 cm^3mol^{-1} to 29.81 cm^3mol^{-1} as the Nd^{3+} ions increases from 0-2.0 mol %. However, the results increase slightly from 29.81 $cm3mol^{-1}$ to 30.75 $cm3mol^{-1}$ as the Nd^{3+} content varies from 2.0-2.5 mol. Overall, the molar volumes are found increases with respect to mol % of Nd^{3+} content. The behavior of molar volume mainly depends upon the density of glasses [8].

3.2 Optical Absorption and Energy Gap

Figure 1 shows the absorption spectra of Neodymium doped Lead Borotellurite glasses. The absorption coefficient $\alpha(\nu)$, was determined near the absorption edge, at different photon energies for all the investigated samples. The quantity $\alpha(\nu)$ can be displayed in a number of ways as described by the relation

$$\alpha(\nu) = B(h\nu - E_g)^n / h\nu \quad (5)$$

where B is a constant, E_g is the optical band gap energy and refractive index can take any value between 0.5 and 3.0 depending on the nature of the inter-band electronic transitions [8]. It has been observed that for indirect allowed transitions the measured absorption fits well to the above relation (5) for n=2. These results are therefore plotted as $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) as shown in Figure 2 to find the values of the optical band gap (E_g). The variation of optical energy band gap values versus Nd_2O_3 mol% is as shown in Figure 3. The E_g decreases up to 1.0 mol% of Nd_2O_3. The change in E_g may be due to the variation of density as well as the creation of bridging oxygen.

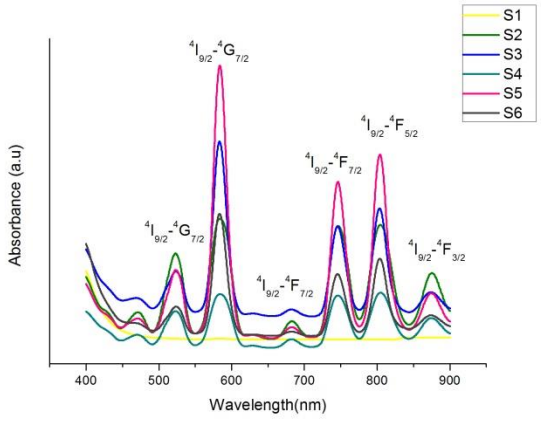


Figure 1 Optical absorption spectra of TeO_2-B_2O_3-PbO glasses

Table 1 Density, molar volume, optical energy band gap, refractive index, molar refraction and polarizability of oxide ion for TeO_2-B_2O_3-PbO glasses

Glass Samples	Density (ρ)(gcm^{-3})	Molar Volume (V_m)(cm^{-3})	Energy band gap (E_g)(eV)	Refractive Index (n)	Molar Refraction (R_M)(cm^3)	Polarizability(α_e) (x10^{-24})(cm^3)
S1	5.119	30.93	2.57	1.89	14.277	5.560
S2	5.136	30.83	2.53	1.90	14.343	5.686
S3	5.235	30.25	2.35	1.96	14.715	5.833
S4	5.240	30.21	2.48	1.92	14.272	5.658
S5	5.310	29.81	2.55	1.90	13.869	5.498
S6	5.149	30.75	2.59	1.89	14.194	5.627

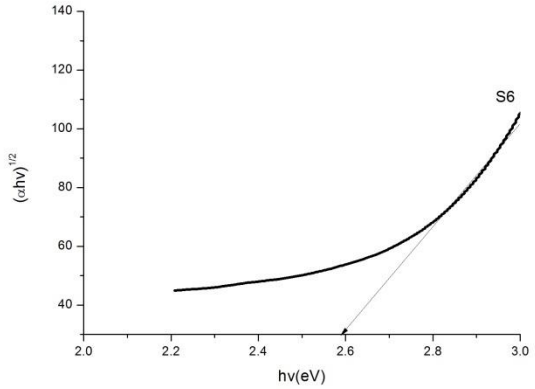


Figure 2 Tauc's Plot of TeO_2-B_2O_3-PbO glasses for sample S6

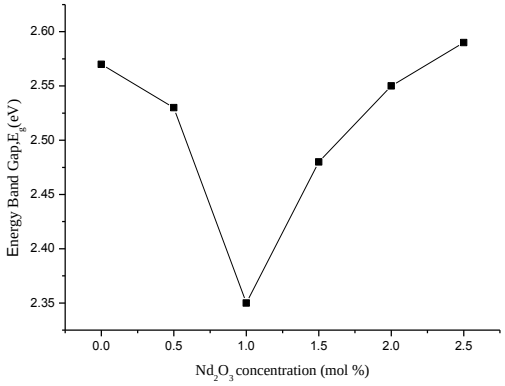


Figure 3 Variation of energy band gap vs Nd_2O_3 in TeO_2-B_2O_3-PbO glasses

3.3 RI, Molar Refraction and Polarizability

Refractive index (n) depends upon the composition of an optical material. Molar refraction (R_M) and 'n' depend on the polarizability of the material. It can be seen from Table 1 that refractive index increases up to 1.0 mol% of Nd_2O_3 and decreases with further increment of Nd_2O_3. The variations of these parameters are explained accordingly.

The index of refraction depends upon the electron density or the polarizability of ions to a large extent. The contribution to the refractive index from the oxygen is of high importance because the ions in any glass are usually anions [9]. In addition, oxygen is mainly responsible for most of the light refraction in undoped glasses [10]. From Figure 4, it is the evident that by the introduction of Nd^{3+} ions in the host glass, refractive index shows increment trends however further addition of Nd^{3+} ions decreases the refractive index and becomes maximum for 1.5 mol% Nd^{3+}. This significant increase in refractive index is probably due to the contribution of non-bridging oxygen (NBOs) since they are strongly polarizable [10]. Furthermore, by the addition of modifier the refractive index can also be enhanced because it usually breaks the Te–O–Te linkages and creates NBOs and electric dipoles contribute to an increase of the refractive index. Therefore refractive index can be varied by using different types of modifier.

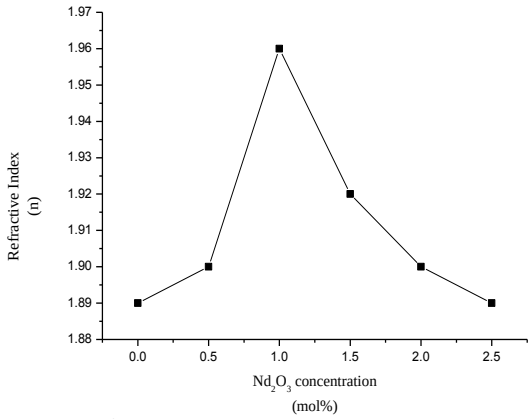


Figure 4 The refractive index against Nd_2O_3 in TeO_2-B_2O_3-PbO glasses

4.0 CONCLUSION

In conclusion, Nd^{3+}-doped lead borotellurite glasses has successfully been synthesized by using conventional melt quenching technique. Glass density and molar volume shows opposite trends as expected. Meanwhile, optical band gap energy decreases up to 1.0 mol% of Nd_2O_3. The addition of modifier makes the linkages between the Te-O-Te bonds breaks up and creates non-bridging oxygen. TeO_2 in the glass network acts as glass former and hence there is a structural change in glass network. The role of Nd^{3+} ions in modifying the structural and optical properties is well understood.

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