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PHYSICAL AND STRUCTURAL STUDIES OF Nd^{3+} DOPED LEAD BORO-TELLURITE GLASSES

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Abstract

Series of glasses with compositions $20PbO–20TeO_2–(60–x)B_2O_3–xNd_2O_3$*(in mol.%) where x= 0, 1,2,3,4 were prepared by melt quenching method. The compositional dependence of different physical parameters such as density, molar volume, polaron radius, optical basicity have been analysed and discussed. The densities and optical basicities are foundbto increase with increase in* Nd_2O_3 *concentration. Optical absorption studies reveal that the values of band gap decrease from 3.508 to 3.314 eV with increase in* Nd^{3+} *concentration. The slight decrease in band gap is due to is due to increase of bonding defect and non-bridging oxygen. It is found that Urbach energy decreases with increase of* Nd_2O_3 *concentration which is attributed to decrease in fragility nature of the glass network. IR studies revealed that the structure of prepared glass network consists of* $[TeO_3]$ / $[TeO_{3+1}]$, $[TeO_4]$, $[BO_3]$, $[BO_4]$ *and B-O-Pb linkages.*

Keywords: Boro-tellurite glasses: Neodymium-doped glasses and UV-Optical.
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1.Introduction

Rare earth doped glasses have attracted a great deal of interest due to their macroscopical properties such as high mechanical resistance, chemical stability and heat- resistance [1]. Nd^{3+} doped glasses have proven to be one of the most efficient candidates for photonic devices such as fiber lasers, micro chip lasers and planar wave guides [2-4]. PbO based glasses have interesting physical properties such as high density, high linear and non-linear refractive index enabling their extensive various applications in optics and optoelectronics [5]. TeO_2 based glasses are known as good hosts for rare earth ions in possible uses for practical laser applications [6]. B_2O_3 is one of the best and well known glass former and is present in almost all commercially important glasses. Boro-Tellurite glasses have been widely studied because of the industrial importance of tellurites in making glasses with desirable optical properties [7].

The Physical properties of glass provide an insight into the atomic arrangements in a glass network. The study of optical absorption edge is useful for understanding the optically induced transition and optical band gaps of materials. IR studies give information about structure of glass composition. These considerations motivated us to study physical properties, optical band gap and structural studies of glass compositions (in mol.%) $20PbO–20TeO_2–(60–x)B_2O_3–xNd_2O_3$ (PTBN)where x= 0, 1,2,3,4.

2. Experimental

The Neodymium oxide (Nd_2O_3) doped lead–tellurite-borate glass samples were prepared by high purity analytical grade chemicals of PbO, H_3BO_3, TeO_2 and Nd_2O_3. These ingredients were thoroughly mixed and melted in a porcelain crucible in an electrical furnace at a temperature of 1150^0C for 30 min. The melt was air quenched by pouring it on a pre-heated brass block at 250^0C and covering it immediately with brass plate. Density of the bubble-free glass samples were measured by employing Archimedes principle using xylene as an immersion liquid. The refractive index of the samples was measured using Abbe′s refractometer with mono-bromonaphthalene as the contact layer between the sample and prism of the refractometer. The light source used was sodium vapor lamp at wavelength 589.3nm. UV-Visible absorption spectra were recorded in the range 300 – 900 nm using Perkin-Elmer spectrophotometer.FT-IR transmission spectra were recorded using Thermo-Nicolet 6700 spectrometer in the range 400-1800cm^{-1}.

3. Result and Discussion

3.1 Physical properties

The formula used to calculate densities of the prepared samples is

$$\rho = \frac{W_a}{W_a - W_b} \text{ x } \rho_b \qquad (1)$$

Where $W_a$the weight in air is, W_b is the weight in xylene and ρ_b is the density of xylene.

Average molecular weight of the multi-component glass system was calculated using the relation

$$M_{av} = X_{PbO}Z_{PbO} + X_{TeO_2}Z_{TeO_2} + X_{B_2O_3}Z_{B_2O_3} + X_{Nd_2O_3}Z_{Nd_2O_3}$$

Where X_{PbO}, X_{TeO_2}, $X_{B_2O_3}$ and $X_{Nd_2O_3}$are the mole fractions of the constituent oxides, and Z_{PbO}, Z_{TeO_2} ,$Z_{B_2O_3}$ and $Z_{Nd_2O_3}$ are the molecular weights of the constituent oxides.

Molar volume (V_M) was calculated using the relation $V_M = \frac{M_{av}}{\rho}$

The number density N i.e., the number of ions per cubic centimetreof the Nd^{3+}ions was calculated using the relation [8]

$$N = \frac{x\rho N_A}{M_{av}} \qquad (2)$$

Where x is the mole fraction of rare- earth oxide, ρ is the density of the glass, $N_A$is Avogadro's number and M_{av} average molecular weight of the glass.

From the known value of N, following three related physical properties were calculated [9].

Polaron radius r_p (Å) $= \left(\frac{1}{2}\right)\left(\frac{\pi}{6N}\right)^{1/3}$ (3)

Imter nuclear distance, r_i(Å) $=\left(\frac{1}{N}\right)^{1/3}$ (4)

Field strength, F (cm^2) $= \left(\frac{Z}{r_p^2}\right)$ (5)

Where Z is the charge of the ion.

The reflection loss from the glass surface was calculated from the refractive index by using Fresnel's formula [10]

$$R\,\% = \left(\frac{n_d-1}{n_d+1}\right)^2 \text{x } 100 \qquad (6)$$

Where n_d is the refractive index of the glass at wavelength 589.3 nm.

The dielectric constant (ε) was calculated from the refractive index of the glass using the formula [11]

$$\varepsilon = n_d^2 \qquad (7)$$

The molar refractivity R_M for each glass was calculated using the relationship [12]

$$R_M = \left(\frac{n_d^2-1}{n_d^2+2}\right)\frac{M_{av}}{\rho} \qquad (8)$$

The optical dielectric constant($P\partial t/\partial P$) was calculated using the formula [13]

$$P\partial t/\partial P = (\varepsilon - 1) = (n_d^2 - 1 \qquad (9)$$

Variation of density and molar volume with Nd_2O_3 concentration is presented in figure 1.It can be observed that the density increases with increase in Nd_2O_3 content. This is attributed due to replacement of lower molecular weight substance B_2O_3 with higher molecular weight of oxide ions Nd_2O_3 in the glass network. This also shows that the addition of Nd_2O_3 results in an extension of glass network.

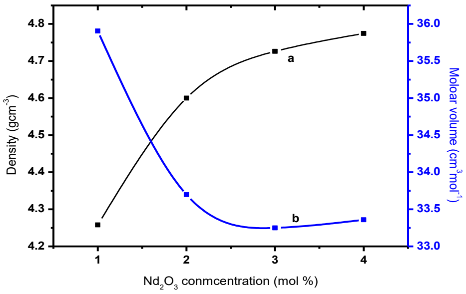


Fig.1. Variation of density and molar volume with Nd_2O_3 concentration.

The results of various physical properties calculated are presented in Table-1.

Table 1 :Physical properties of Nd^{3+}doped PTB glasses

Physical property	PTBN1	PTBN2	PTBN3	PTBN4
Density, ρ (g/cm^3)	4.258	4.600	4.726	4.774
Optical path length (cm)	0.165	0.193	0.181	0.180
Refractive index,(n_d) at 589.3nm	1.420	1.440	1.460	1.490
Average Molecular weight,M_{av}(g)	152.881	155.010	157.138	159.266
Molar volume, V_M (cm^3)	35.899	33.696	33.248	33.359
Nd^{3+}-ion concentration, N ($\times 10^{20}$ ions/cm^3)	1.677	3.574	5.434	7.2303
Polaron radius, r_p (Å)	7.308	5.676	4.938	4.490
Inter nuclear distance, r_i(Å)	18.135	14.152	12.254	11.141
Field strength, F ($\times 10^{15}$cm^{-2})	0.561	0.931	1.230	1.668
Reflection loss, R %	3.012	3.251	3.496	3.872
Dielectric constant,ε	2.016	2.073	2.131	2.220
Molar refractivity, R_M (cm^3)	9.0084	8.880	9.1063	9.642
Optical dielectric constant , $P\partial t / \partial P$	1.016	1.073	1.131	1.220

The polaron radius is found to decrease with the increase in neodymium oxide content. This result agrees with literature [14]. As expected the intermolecular distance for rare earth ions shows an expected decrease on increasing Nd_2O_3 content. The molar refractivity, which depends on the refractive index, density and average molecular weight of glass, shows minimum around 2 mol% of Nd_2O_3. This agrees with results reported in literature [15]. The data presented in Table 1 show that an increase in the average molecular weight influences significantly both the density and also other physical quantities. The variation of physical quantities with increase in Nd_2O_3 content agree with reported in literature [10].

3.2 Optical band gap

Room temperature the UV-Visible absorption spectra of Nd^{3+} doped glass system is as shown in Figure 2. The absence of sharp peaks in the absorption spectra corresponds to characteristics of amorphous nature. It is observed that the absorption intensity of the observed bands increases with increases of Nd_2O_3 concentration.

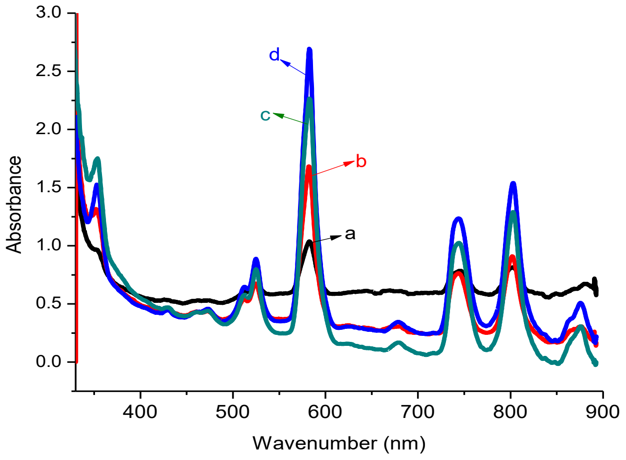


Fig.2. UV-Visible absorption spectra (a) PTBN1(b) PTBN2 (3) PTBN3 (d) PTBN4 glasses.

In order to study the optically induced transitions, optical band gaps have been computed from the UV-Visible absorption spectra of the glasses. The optical absorption at the fundamental edge in terms ofthe theory given by Davis and Mott [16] in the generalform is

$$\alpha(\nu) = \frac{B}{h\nu}\left(h\nu - E_{opt}\right)^{n} \qquad (10)$$

This relation can be written as

$$(\alpha h\nu)^{\frac{1}{n}} = B\left(h\nu - E_{opt}\right) \qquad (11)$$

Where B is a constant called band tailing parameter, $h\nu$is the photon energy and E_{opt} is the optical energy gap. Values of n are 1/2 and 2 for direct and indirect forbidden transitions, respectively.

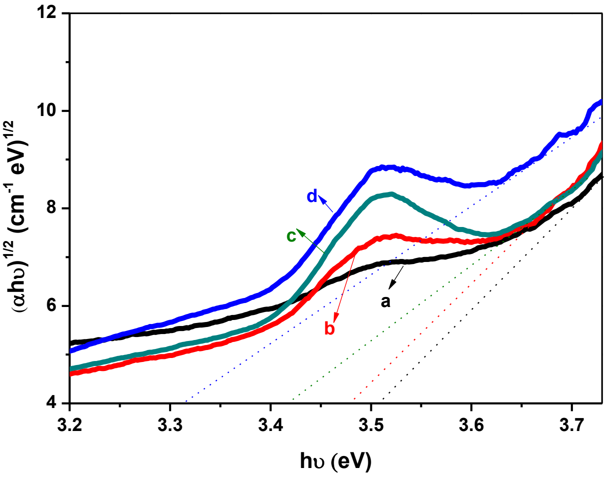


Fig.3. Tauc's plot for (a) PTBNI, (b) PTBN2, (c) PTBN3 and (d) PTBN4 glasses.

The absorption coefficients$\alpha(\nu)$were determined near the absorption edge at different photon energies (hν) for all glass samples. It is observed that for many amorphous materials, a reasonable fit of equation (10) with n=2 are achieved. Therefore the typical plot of $(\alpha h\nu)^{1/2}$ versus photon energy hν (Tauc's plot) is plotted and it is as shown in figure 3 for indirect allowed transitions. The values of band gap obtained are3.508, 3.480, 3.420, and 3.314 eV for PTBN1, PTBN2, PTBN3 and PTBN4 respectively. It can be observed that the optical band gap slightly decreases with the increase of Nd_2O_3 concentration and results in the increase of bonding defect and non-bridging oxygen. This leads to an increase of the degree of the localization of electrons there by the increase of donor center in the glass matrix. The increase of presence of donor centre leads to the decreases of optical band gap, therefore, the shift of absorption edge toward the longer wavelength was observed.

To calculate the width of energy tail, ΔE, of the density of states, the model proposed by Urbach.andTauch . The following relation has been used to determine the width of the energy tail.

$$\ln\alpha = C + \frac{h\nu}{\Delta E} \quad (12)$$

Where C is a constant.

Urbach plots are the plots where natural logarithm of absorption coefficients ($\ln\alpha$) is plotted against photon energy (hν). The Urbach plot for Nd^{3+} doped PTB glasses is presented in Figure 4.

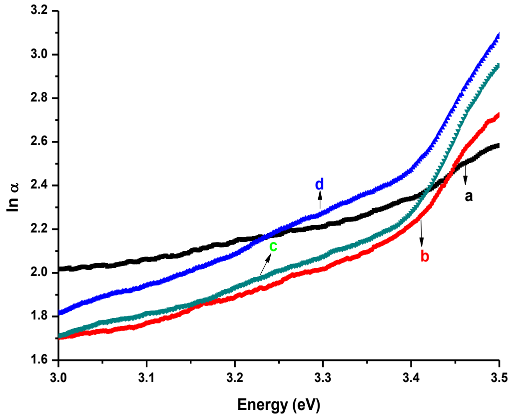


Fig. 4.Urbach plot for (a)PTBN1 (b) PTBN2 (c) PTBN3 and (d) PTBN4 glasses.

The values of Urbach energy were calculated by determining slopes of the linear regions of the curves and taking their reciprocals. The values of Urbach energies obtained are O.352, 0.2029, 0.1347 and 0.1159 eV for (a) PTBN1 (b) PTBN2 (c) PTBN3 and (d) PTBN4 glasses respectively. It is found that Urbach energy decreases with increase of Nd_2O_3 concentration which is attributed to decrease in fragility nature of the glass network.

3.3 Optical basicity of the glasses

Theoretical optical basicity (Λ_{th}) serves in the first approximation as a measure of the ability of oxygen to donate a negative charge in the glasses. Theoretical optical basicity for the multi-component glass system has been calculated by using basicity assigned to the individual oxides on the basis of the following equation proposed by Duffy and Ingram[. For the present glass system

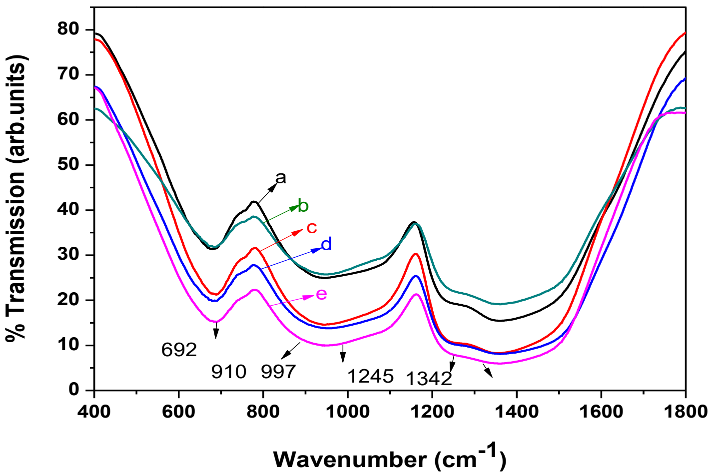
$$\Lambda_{th} = x_1(PbO)\Lambda_1(PbO) + x_2(TeO_2)\Lambda_2(TeO_2) + x_3(B_2O_3)\Lambda_3(B_2O_3) + x_4(Nd_2O_3)\Lambda_4(Nd_2O_3) \quad \text{........(13)}$$

Where$x_1(PbO)$, $x_2(TeO_2)$, $x_3(B_2O_3)$ and $x_4(Nd_2O_3)$ are the equivalent fractions of different oxides, i.e. the proportion of the oxide atom they contribute to the glass system and $\Lambda_1(PbO)$, $\Lambda_2(TeO_2)$, $\Lambda_3(B_2O_3)$ and $\Lambda_4(Nd_2O_3)$ are optical basicity values assigned to the constituent oxides taken from the literature .

The calculated values of optical basicity are 0.6822, 0.6875, 0.6928 and 0.6980 for PTBN1, PTBN2, PTBN3 and PTBN4 glasses respectively. It can be observed that optical basicity increases with an increase of Nd_2O_3 concentration. It may be due to the fact that Nd_2O_3 is having larger basicity (0.9501) than B_2O_3 (0.425). The increase of optical basicity in the present matrix shows ability of oxide ions to transfer electrons to the surrounding cations.

3.4 FTIR Spectra

The infrared transmittance spectra of the present glass system in the region 400-1800cm^{-1} region have large, medium, weak and broad peaks (Fig.5).



Fig, 5.IR spectra of (a)PTBNO (b) PTBN1(c) PTBN2 (d) PTBN3 and (e) PTBN4 glasses.

A literature survey indicates that the vibrational modes of the borate network are mainly active in the three infrared spectral regions. A region around 600-700cm^{-1} due to the bending of the B-O-B linkage in BO_3 group, another region in 800-1200 cm^{-1}due to the B-O bond and a region in 1200-1600 due to stretching of the trigonal BO_3 units .

The structural bands of the present glass system is characterized by IR absorption bands in the wave numbers region 400-600 cm^{-1}, 633-646cm^{-1} , 677-688cm^{-1}, 756-767 cm^{-1}, 910-933cm^{-1}, 1245-1252 cm^{-1} and 1342-1360 cm^{-1}.

The IR band positions are summarized in Table 2.

Table 2 IR band assignments for the Nd^{3+}undoped and doped PTB glasses.

Characteristic IR bands in cm^{-1}	Assignment
633-646	Te-O-Te linkages
677-688	Stretching vibrations of TeO_2trigonal by pyramidal
756-767	Stretching vibrations of TeO_3tp
910-933	B-O-B bending vibrations in BO4 units
~ 997	Stretching vibrations of B-O-Pb linkages
1245-1252	Asymmetric stretching vibration of B-O bonds from ortho borate groups
1342-1360	B-O bonds stretching vibrations of BO_3 units from various borate groups

Intense absorption bands or weak shoulders in the region 633-767cm^{-1} correspond to TeO_4.TeO_3/ T_3O_{3+1} units are preserved in all the studied glasses. In the region 600-800 cm^{-1}, B-O-B bending vibrations manifest themselves. The peaks in the region 910-933 $cm^{-1}$are assigned to [BO_4] units, those at 1245-1252$cm^{-1}$are assigned to B-O stretching vibrations in BO_3 units from Boroxol rings and peaks in the regions 1342-1360$cm^{-1}$are assigned to B-O^- stretching vibrations in [BO_3] units from various types of borate groups[17-19]. The shoulder at 997 cm^{-1} is due to stretching vibrations of B-O-Pb linkages. IR studies revealed that the structure of prepared glass network consists of [TeO_3] / [TeO_{3+1}], [TeO_4], [BO_3], [BO_4] and B-O-Pb linkages. There is no change in the structure due to the addition of Nd_2O_3.

4. Conclusions

Nd^{3+} doped Lead-Borate –Tellurite glasses have been successfully prepared and their physical and structural properties have been studied and analyzed. Density increases with increase in Nd_2O_3 content. This is attributed due to replacement of lower molecular weight substance B_2O_3 with higher molecular weight of oxide ions Nd_2O_3 in the glass network. Optical basicity increases with increase of Nd_2O_3 concentration. It may be due to the fact that Nd_2O_3 is having larger basicity (0.9501) than B_2O_3 (0.425). Increase of Nd_2O_3 concentration results in decrease of optical band gap owing to increase in non-bridging oxygen ions shifting the band edge to longer wavelength. Analysis of IR spectra shows that the structure of prepared glass network consists of $[TeO_3]$ / $[TeO_{3+1}]$, $[TeO_4]$, $[BO_3]$, $[BO_4]$ and B-O-Pb linkages.

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