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Optical Properties of Nd^{3+} Doped Sodium-Diborate Glasses Containing Heavy Metal Ions

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Abstract— *There has been an increasing interest in the development of trivalent neodymium ion (Nd^{3+}) doped glasses for photonic devices viz: solid state visible and near IR lasers, frequency converters, up converters, wave guides, fibre amplifiers etc. We have prepared Nd^{3+} doped $Na_2B_4O_7$ – PbO Glasses by melt quenching method. The samples were characterized by XRD and DSC studies. The glass transition temperature increases with Nd_2O_3 content. This paper reports on physical and optical properties of Nd^{3+} doped lead-diborate glasses. In the case of Nd^{3+} ion, the absorption takes place from the ground state $^4I_{9/2}$ to various excited states which are predominately 4f-4f induced electric dipole in nature. On the basis of the measured values of density, molar volume and optical band gaps, the refractive index, Nd^{3+} ion concentration, electronic polarizabilities, polarizabilities of oxide ions and optical basicity were estimated and the results were analyzed on the basis of the structural modifications occur in the glass.*

Keywords— *Density, Optical band gap, Polarizability, Optical basicity and photoluminescense.*

1. INTRODUCTION

Rare earth doped glasses have been studied with the aim to utilize their fluorescence properties. [1]Optically transparent glasses containing ferro electric and nanocrystals have received much interest as such materials can be used as Laser host materials, tunable wave guides or tunable fiber gratings [2]. The scientific interest of glasses containing Nd^{3+} have gained importance after the demonstration of lasing action in Nd^{3+} -doped glasses by Snitzer [3]. There has been an increasing interest in the development of trivalent neodymium ion (Nd^{3+}) doped glasses for photonic devices viz; solid state visible and near IR lasers, frequency converters, up converters, wave guides, fiber amplifiers etc. [4-9]. Borate glasses are suitable for optical materials because of their high transparency, high thermal stability, different coordination numbers, and good solubility of rare-earth ions [10–12]. Further, heavy metal oxide glasses posses reduced phonon energy, high density, high refractive index, optimum band width, high mechanical and thermal stability, corrosion resistance and good solubility of rare earth ions. Thus, the incorporation of heavy metal oxides such as PbO or Bi_2O_3 into the borate glass matrix gives good luminescence properties of rare-earth ions in excited states. Further, it is well established that the addition of an alkali oxide has a strong influence on the boron coordination and the structural groups, depending on the type and concentration of the alkali oxide [13]. However, to the best of our knowledge, Nd^{3+} doped lead sodium diborate glasses have not been studied in any great detail. Motivated by these considerations, in this paper we have prepared lead - sodium diborate glasses doped with Nd^{3+}ions, and studied the effects of the Nd^{3+} concentration on physical and spectroscopic properties.

2. EXPERIMENTAL

The glass samples having the general chemical formula 30PbO - (70-x) $Na_2B_4O_7$ –x Nd_2O_3 with x=0, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 mol% have been prepared by the melt quenching technique. Required quantities of annular grade PbO, Na_2CO_3, H_3BO_3 and Nd_2O_3 were mixed together by grinding the constituents repeatedly to obtain an isotropic mixture. The mixture was melted in a porcelain crucible in an electrically heated mupple furnace under ordinary atmospheric conditions at a temperature of about 1000^0C for 1 h to homogenize the melt. The glass formed by quenching the melt between two pre-heated brass plates. The glass samples were annealed at 200^0C for 2 h to remove any thermal stresses that could have formed during the fast quenching process and the glasses were preserved under anhydrous atmosphere. The amorphous nature of the glass samples were confirmed using podered X-ray diffraction (Model: Rigaku DMAX- IC employing Cr-K radiation). The XRD spectra did not show any sharp peaks, indicating that the samples were amorphous in nature. The densities of the

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synthesized glasses were measured at room temperatures by applying Archimedes principle, with toluene as the immersion liquid. Molar volume was calculated for each sample using the relation, V=M/ρ, where M is the molecular weight calculated according to the relation M= $\Sigma x_i m_i$ (x_i is the mole fraction of the component oxide and m_i is its molecular weight). UV–Visible Absorption spectra of synthesized glasses was recorded using Perkin Elmer (Lamda 35) spectrometer in the UV-Vis-NIR region in the range 200 to 1000 nm.

3. RESULTS AND DISCUSSION

Density and Molar volume— The Sample codes, composition and average molecular weights are tabulated in Table 1. The variation of the density and molar volume with Nd_2O_3 concentration is shown in Fig. 1. As can be seen in Fig.1, both the density and molar volume increases with the increase of Nd_2O_3 mol%. This indicates that replacing $Na_2B_4O_7$ by addition of a small amount of Nd_2O_3 results in the increase in the average molecular weight of oxide ions in the glass.

Table 1: Sample codes, composition and average molecular weights

Sample Code	*Sample composition in mol%*			*Molecular weight M (gm)*
	$Na_2B_4O_7$	*PbO*	*Nd_2O_3*	
0NDP	70.0	30	0.0	113.87
1NDP	69.8	30	0.2	114.40
2NDP	69.6	30	0.4	114.94
3NDP	69.4	30	0.6	115.48
4NDP	69.2	30	0.8	116.02
5NDP	69.0	30	1.0	116.56
6NDP	58.0	30	2.0	119.26

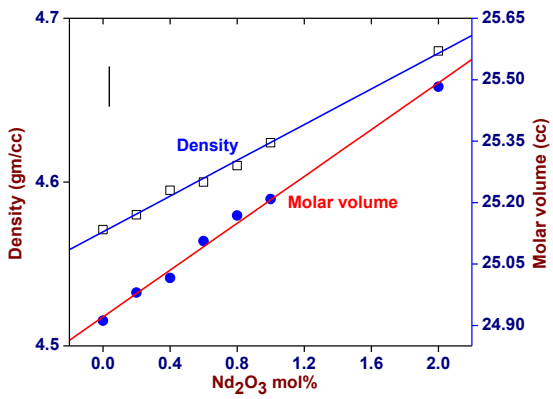

Fig. 1: Variation of density and molar volume with Nd_2O_3 mod%

Also Nd_2O_3 has a higher relative molecular mass compared to $Na_2B_4O_7$. Based on the measured density, the Nd^{3+}-ion concentration and other related physical properties such as polaron radius, inter nuclear distance and field strength can be determined using Eqs. in reference [14] and the results are tabulated in Table 2.

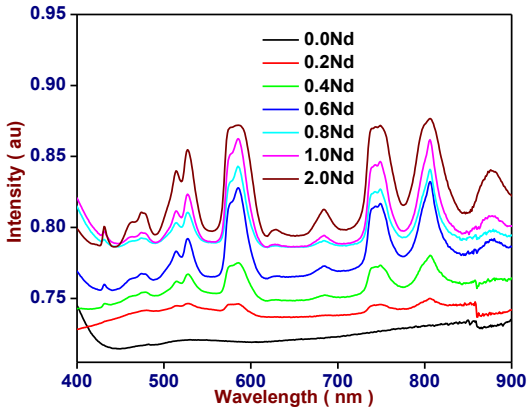

Fig. 2: UV-Visible spectra of Nd^{3+} doped PbO-$Na_2B_4O_7$ glass system

Table 2: Nd^{3+} concentration(N), polaron radius (r_p), internuclear distance(r_i) and field strength (F).

Code	*$NX10^{22}$ Ions/cc*	*r_p A^0*	*r_i A^9*	*$FX10^{15}$ (cm^{-2})*
0NDP	-	-	-	-
1NDP	0.4822	11.069	27.471	0.2448
2NDP	0.9620	8.793	21.823	0.3879
3NDP	1.4395	7.688	19.081	0.5079
4NDP	1.9145	6.991	17.351	0.6138
5NDP	2.3872	6.495	16.122	0.7111
6NDP	4.7270	5.172	12.837	1.1213

Generally, as density increases the molar volume decreases. In the present glass system both the density and molar volume increases as a function of Nd_2O_3 concentration. The increase in molar volume could be due to the modifying role of Nd_2O_3.As concentration of Nd_2O_3 increases, the tightly packed diborate units opens up. Consequently, the non bridging oxygen's in the glass network increases.

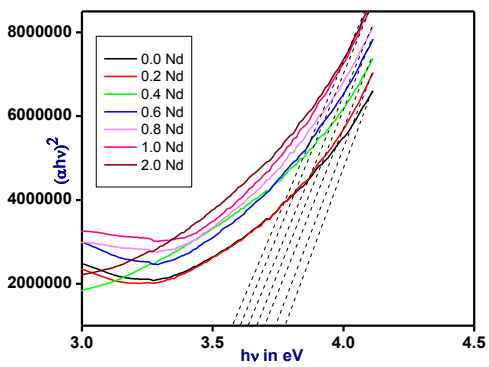

Fig. 3: Direct band gap plots of Nd^{3+} doped $Na_2B_4O_7$-PbO glass system

UV-Visible Absorption Spectra— The UV-Visible absorption spectrum of Nd^{3+} doped lead-sodium-diborate glasses is shown in the figure 2. The optical absorption edges are not sharply defined in glass samples under study, in accordance with their amorphous nature [15]. From this spectrum, It is observed that the absorption intensity of the observed bands increase with an increase in Nd_2O_3 concentration. The spectra consists of various absorption bands at 472 nm, 511 nm, 524 nm, 583 nm, 624 nm, 686 nm, 745nm, 802 nm and 874 nm are identified and these are assigned to the electronic transitions $^4I_{9/2} \rightarrow {}^2G_{9/2}$, $^4G_{9/2}$, $^4G_{7/2}$, ($^4G_{5/2}$ + $^2G_{7/2}$), $^4F_{9/2}$, ($^4S_{3/2}$ + $^4F_{7/2}$), ($^4F_{5/2}$+$^2H_{9/2}$) and $^4F_{3/2}$ respectively. Assignments to these bands have been made by using the reference [16]. For the absorption region, Mott and Davis proposed the following relation for amorphous materials [17]

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

Where B is a constant and n= ½ allowed transition gives direct optical band gap, n=2 allowed transition gives indirect optical band gap. By plotting $(\alpha h\nu)^2$ as a function of photon energy $h\nu$, optical band gaps for direct transitions could be found respectively by extrapolating to $(\alpha h\nu)^2 = 0$ for direct transitions. similarly indirect band gaps could be estimated by plotting $(\alpha h\nu)^{\frac{1}{2}}$ as a function of photon energy $h\nu$. The typical plots of $(\alpha h\nu)^2$ v/s $h\nu$ for glass samples sample to calculate direct band gaps are shown in fig 3. The absorption coefficient, below and near the edge of each curve was determined at different wavelengths using relation

$$\alpha(\gamma) = \frac{1}{d}\ln\left(\frac{I_o}{I_t}\right)$$

Where I_0 and I_t are intensities of incident and transmitted beams, respectively and d corresponds to thickness of each sample.

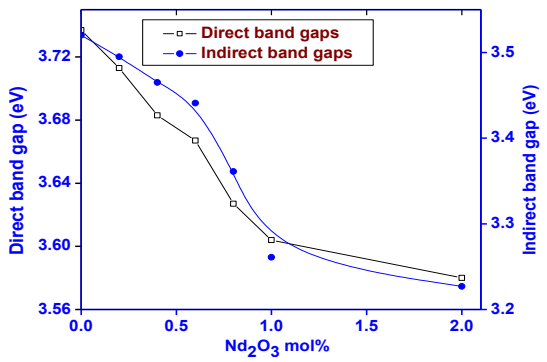

Fig. 4: Variation of optical band gaps with N d_2O_3 mol%

The graph of optical band gaps as a function of Nd_2O_3 is shown in Fig.4. It is depicted from Fig 4 that the optical band gap energy decreases with the addition of Nd_2O_3 may be due to structural modifications. Addition of Nd_2O_3 may lead to an increase in the degree of electron concentration and thereby the increase of donar centres in the glass matrix. From the direct energy band gaps, refractive index of the samples has been calculated using the relation $n = \alpha + \beta E$. Where α = 4.68 eV, β = -0.62 eV and E is the band gap energy. Glass optical basicity (Λ) and from refractive index values, Molar polarizability (α_m), Glass oxide polarizability (α_o^{2-}) have been estimated using the formulae given in reference [18] and are listed in Table 3.

Table 3: Molar polarizability α_m (Å^3), Glass oxide polarizability α_o^{2-}(Å^3) and Glass optical basicity (Λ) values

CODE	α_m Å^3	α_o^{2-} Å^3	*Λ*
0NDP	4.0798	1.5022	0.5903
1NDP	4.1507	1.5326	0.5927
2NDP	4.2290	1.5670	0.5952
3NDP	4.2830	1.5887	0.5976
4NDP	4.3892	1.6371	0.6001
5NDP	4.4505	1.6626	0.6025
6NDP	4.5566	1.6858	0.6146

From the Table 3 it is noted that, optical basicity, molar polarizability and oxide polarisability values increases with increase in Nd_2O_3 mol%. This clearly establishes the fact that covalency in the glasses decreases with the increase of Nd_2O_3 mol% which correlates with the decrease in optical gaps.

4. CONCLUSION

Nd^{3+} doped lead-sodium diborate glasses have been synthesized to study physical and optical properties. The properties such as density, molar volume, optical band gaps, refractive index, polarisabilities, and optical basicity of the glass reveals the structural changes occurred due to the network modifying role played by the rare earth oxide (Nd_2O_3). As concentration of Nd_2O_3 increases, the population of NBO's in the network increases. Consequently the degree of electron localization and donor centers in the structure increases.

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