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ABSORPTION SPECTRA OF NEODYMIUM DOPED LITHIUM NIOBIUM BORATE GLASS

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ABSTRACT

A series of (90-x)$Li_2B_4O_7$-10Nb_2O_5-xNd_2O_3 glass composition has been synthesized with mole fraction x = 0, 10, 15, 20 and 25 mol % using melt quenching technique. The amorphous natures of the glass were confirmed from x-ray diffraction (XRD) pattern. The glass densities are found to be increased whereas the molar volumes are decreased with respect to the Nd^{3+} content. The absorption spectra of these glasses were recorded a number of absorption bands in ultra violet and visible region to determine the optical energy gap and Urbach energy. The values of the optical band gap are found to lie between 2.97 to 3.82 eV, while the Urbach energy values vary is between 0.163 and 0.413 eV. It was found that the optical energy gap for indirect forbidden transition and values of Urbach energy has increased except for sample 20NdLNB with the increasing of Nd_2O_3 content. The structural and optical properties were found to be strongly affected by the varying concentration of Nd^{3+} ions.

Key Word: Borate glass; neodymium; optical band gap; Urbach energy

INTRODUCTION

The research interest in borate glass system is because of the anomalous behaviour of these glasses. In comparison with other conventional glasses, borate glass is a most recently studied due to their good optical and mechanical properties. Borate is well known to be good in mechanical strength and chemical durability, stable against atmospheric moisture, good solubility of rare earth (RE) ions, low melting temperature and good in corrosion resistance [1-3]. Lithium acting as modifier can reduce the hygroscopic nature of borate and improve the stability by forming ionic bonds with oxygen (non-bridging oxygen). These bonds are responsible for formation of color centers [4]. Several alkaline and alkali earth metals are used as a second modifier to alter the glass structures, to open up the network structure, to reduce bond strength and to minimize the stickiness of the glass [5-7].

Modifying the optical properties of glasses by controlling rare earth doping is an important issue. The optical absorption was utilized to study the shape and shift of the absorption edge. It is very useful method to understand the mechanism of optically-induced transitions and the information about the band arrangement in crystalline and non-crystalline materials also can be obtained. A photon with greater energy will absorb the principle of this method compared the band gap energy [8]. It has become an important tool in studying the absorption of glasses for many decades.

Broad research on rare earth containing glasses has been investigated widely because of their direct application in optical communications, optical storage devices, laser technology and immobilization of radioactive materials [9–12]. These rare earth containing glasses shows good mechanical strength, chemical and thermal stability. The optical absorption spectra of glasses containing Nd_2O_3 is in ultraviolet to infrared region which overlap well with high- brightness pump sources in the UV and visible range. The output wavelength in the vicinity of 1.6 μm is of interest for laser application [13]. Nd^{3+} shows large emission cross section corresponding to the 4F3/2→4I11/2 around 1064 nm [14]. The main objectives of the present work were to study the role of Nd^{3+} ions on the optical band gap and Urbach energy of the lithium niobium borate glass.

METHODS

Glasses with chemical compositions in mol % (90-x)$Li_2B_4O_7$-10Nb_2O_5-xNd_2O_3, where x = 0, 10, 15, 20 and 25, defined as LNB (base glass),

10NdLNB, 15NdLNB, 20NdLNB, and 25NdLNB respectively were prepared by melt-quenching technique. Batches of 20g were prepared from certified reagent grades of $Li_2B_4O_7$ (99.95% purity), Nb_2O_5 (97%), and Nd_2O_3 (99.995%). The chemicals were firstly mixed thoroughly in a platinum crucible before being heated at 1150°C for 1hour. After the batch was completely melted, the melts was cast onto the preheated stainless steel plate followed by annealing at 400°C for 5 hours before allowed to cool down to room temperature. The prepared samples were then grinded and polished until the appropriate thickness achieved. The thickness of glass samples used for optical studies is around 1.1-1.5mm. The structural characterizations are made by x-ray diffraction (XRD). Optical absorption spectra of glasses were recorded at room temperature using UV-VIS-NIR spectrometer (Model–Shimadzu UV-3101PC) in the range of 200–1800nm. The glass density (ρ in g cm^{-3}) is determined using Archimedes method with distilled water as an immersion fluid following the relation:

$$\rho = \rho_\ell \frac{W_A}{W_A - W_\ell} \quad (1)$$

where, WA is the weight of the sample in air, Wt is the weight in the immersion fluid and ρt is the density of the distilled water (1.00 gcm^{-3}). Meanwhile, the molar volume, Vm is calculated using the relation:

$$V_m = \frac{M}{\rho} \quad (2)$$

The optical absorption coefficient α(λ) were calculated using the equation:

$$\alpha(\lambda) = 2.303 \frac{A}{d} \quad (3)$$

where A is absorbance and d is the sample thickness.

RESULT AND EXPLANATION

The samples obtained are observed to have good quality. From the observation, it was found that the presence of Nd^{3+} ions in the glass system tend to alter the coloration of the glass from light purple to dark purple. This indicates the uniform distribution of Nd^{3+} ions in the glass matrix.

Figure 1 shows the XRD spectra for LNB and 10NdLNB samples. Both samples show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is clear indication of amorphous nature of glass structure.

The density (ρ) and molar volume (V_M) of glasses are important parameters to study since slight change in glass structure results in abrupt change in density.

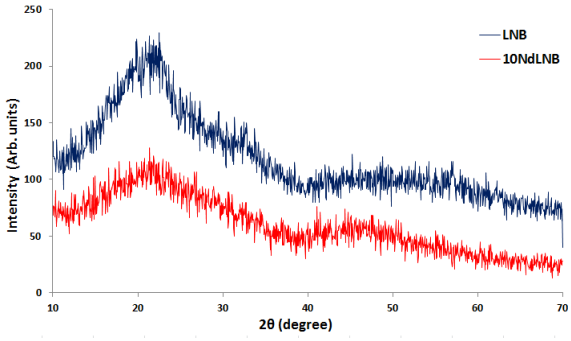


Figure 1 The XRD spectra for LNB and 10NdLNB

On the other hand distribution of the oxygen in the glass structure can be understood on the basis of molar volume. The values of density and molar volume of the glass are listed in Table 1. Figure 2 shows variation of density and molar volume with respect to Nd_2O_3 content. Glass density is found to increase from 2.84 to 3.38 g cm^{-3} and molar volume is decreased from 68.79 to 62.08 cm^3 mol^{-1} with the increase of Nd^{3+} concentration. The molecular mass of Nd_2O_3 (336.48) being higher than $Li_2B_4O_7$ (169.12) contributes to elevated packing density. The increase number of oxygen atoms increases cation radius. The introduction of Nd^{3+} acquiring higher charges and coordination number tend to develop tightly packed glass structure and thus, increase the density [15]. However, the decrease in the molar volume as function of Nd^{3+} concentration may be due to the reduction of total volume size that contributes to the compactness of the glass which is reduced.

Table 1 Density and molar volume of the glass system

Glass Sample	Density (g cm^{-3})	Molar volume (cm^3 mol^{-1})
LNB	2.88	62.08
10NdLNB	2.84	68.79

15NdLNB	3.02	67.45
20NdLNB	3.24	65.58
25NdLNB	3.38	65.23

Figure 3 illustrates variation of linear absorption coefficient of the prepared glasses. It can be seen from this figure that there are number of absorption bands observed as compared to base glass which corresponds to f-f electronic transition of Nd^{3+} ions. The bands observed are $^4D_{3/2}$ (353 nm), $^2P_{1/2}$ (430 nm), $^2G_{9/2}$ (475 nm), $^4G_{7/2}$ (524 nm), $^4G_{5/2}$ (583 nm), $^4F_{9/2}$ (681 nm), $^4F_{7/2}$ (745 nm), $^4F_{5/2}$ (803 nm) and $^4F_{3/2}$ (875 nm). Our observation of absorption bands are in good agreement with by Ramteke [16] and Renuka [17]. It is also observed from Figure 3 that there is an increase in absorption with the addition of Nd_2O_3. The fundamental absorption edge in the material is due to electronic transition across the conduction and valence band in the material [17–19], therefore it is important to study UV absorption edge.

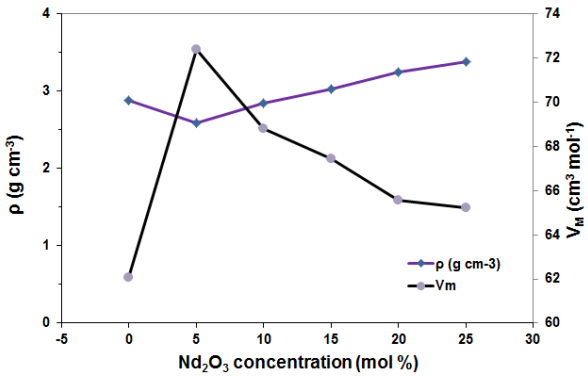


Figure 2 Compositional variation of density and molar volume for Nd_2O_3 doped lithium niobium borate glasses

Figure 4(a) and 4(b) shows the dependence of $(\alpha\hbar)1/2$ and ln α versus $\hbar$ obtained from:

$$\alpha(\omega) = \frac{const}{\hbar\omega}(\hbar\omega - E_{opt})^n \quad (4)$$

where, Eopt is the energy of the optical band gap and $\hbar$ is the photon energy. The n value is 2 for indirect transitions. It is found that most amorphous material best fit with n=2 gives reasonable fit to Equation 2, representing the indirect allowed band transition [20,21]. The interactions of photons with lattice vibrations will take place at this allowed indirect transition. The value of Eopt can be obtained by extrapolating the linear part of the $(\hbar)$/ versus phonon energy, $\hbar$ graph to the axis shown in Figure 4(a). The indirect optical band gap was found to increase from 2.97 to 3.82 eV as increasing the content of Nd_2O_3 which agrees with findings of El-Mallawany et. al [22].

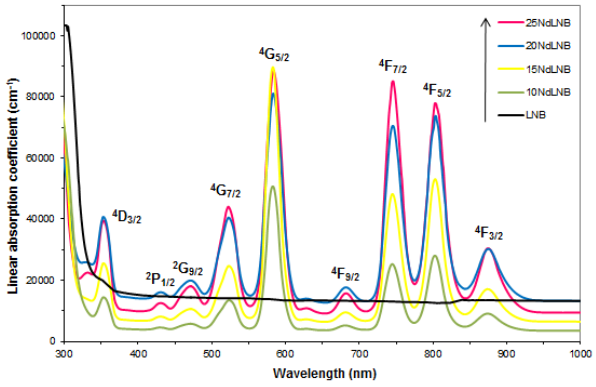
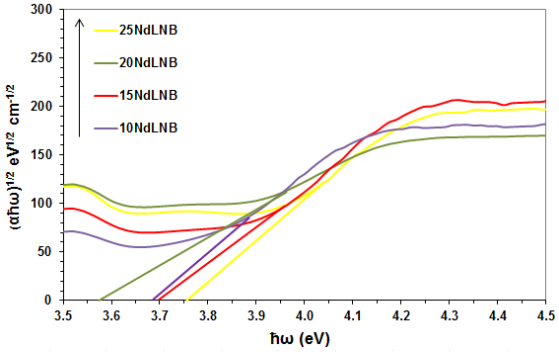


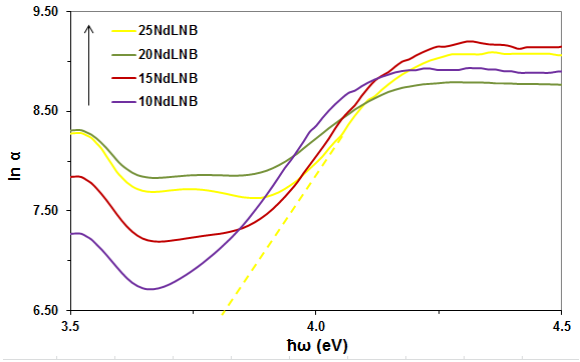
Figure 3 Linear absorption spectra of prepared glasses

Structural disorder in amorphous solid form localized density state within the band tail and leave strong influence on physical and optical properties. Exponential increase of the absorption coefficient with photon energy is the main feature of absorption edge of glasses [23,24]. The increase in absorption coefficient associated with decay of localized density state into the gap when incident photon energy is less than band gap. The absorption edge in this region is called Urbach energy (lie in between 10 and 103 cm^{-1}) [23]. In the Urbach region transition take place between localized band tail and extended conduction band [25,26]. Urbach energy is expressed in terms of following empirical formula [21,23]:

$$\alpha(\omega) = B\exp(\frac{\hbar\omega}{\Delta E_g}) \quad (5)$$



(a)



(b)

Figure 4 (a) Plot of $(\alpha\hbar\omega)^{1/2}$ vs $\hbar\omega$ for indirect band gap of the glass system (b) Plot of ln α vs $\hbar\omega$ for Urbach energy of the glass system

where, B is a constant and ΔE is the width of the band tail of the electron states. From Figure 4(b), Urbach energy is determined from the slope of plot ln (α) versus $\hbar$. The Urbach energy value for glass system was found to lie between 0.163 and 0.413 eV. According to Sreekanth [27], a higher number of defects is due to the increasing the Urbach energy. Therefore, the decrease in the Urbach energy confirms that the numbers of defects are less.

Figure 5 shows that the optical band gap energy, E_{opt} increases with Nd_2O_3, whereas the Urbach energy shows steady decrement, both are except for sample 20NdLNB. This observation is attributed to the formation of non-bridging oxygen. The values of the optical band gap are found to lie between 3.56 - 3.80 eV while, the calculated value of Urbach energy lies between 0.16-0.42 eV as presented in Table 2.

Table 2 Indirect optical band gap, E_{opt} and Urbach energy, E_g of (90-x)$Li_2B_4O_7$-10Nb_2O_5-xNd_2O_3 glass system

Glass Sample	Mol fraction (mol %)			Optical band gap E_{opt} (eV)	Urbach energy, ΔE (eV)
	Nd_2O_3	$Li_2B_4O_7$	Nb_2O_5		
LNB	0	90	10	3.57	0.193
10NdLNB	10	80	10	3.69	0.186
15NdLNB	15	75	10	3.76	0.163
20NdLNB	20	70	10	3.56	0.413
25NdLNB	25	65	10	3.80	0.217

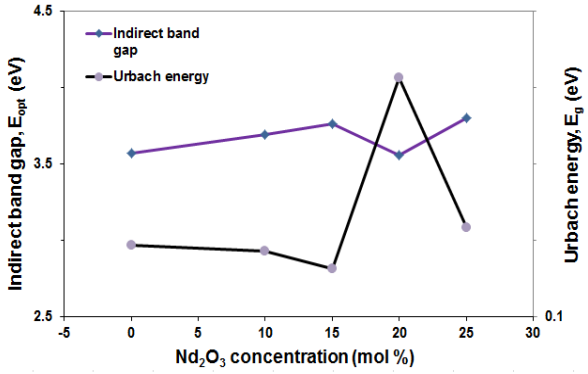


Figure 5 The optical band gap energy, E_{opt} and Urbach energy, E_g of the glass system

CONCLUSION

A series of $Li_2B_4O_7$-Nb_2O_5 glasses with different Nd_2O_3 concentration has been prepared by melt quenching technique and the amorphous nature was confirmed by XRD. Physical parameters such as density and molar volume are found to strongly depend on Nd^{3+} concentration. The optical absorption in UV-VIS-NIR has been studied. The optical absorption spectra in the range of 300-1000 nm display nine bands with significant enhancement as a function of increasing Nd^{3+} contents. The samples show a wide transparency in the UV range. The increase in gap energy for indirect transitions up to 25 mol% of neodymium ions is attributed to the structural alterations. It was found that the optical energy gap for indirect forbidden transition increased, whereas values of Urbach energy has decreased except for sample 20NdLNB with the increasing of Nd_2O_3 content. The Urbach energy is found to be 0.163-0.413eV. The role of Nd^{3+} ions in modifying the structural and optical properties has been understood.

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