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Nd^{3+} CONCENTRATION DEPENDENT OPTICAL FEATURES OF GADOLINIUM BOROPHOSPHO-TELLURITE GLASSES

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ABSTRACT

Improving the optical response of glass host with two or more strong network formers via suitable controlled of rare earth ions is the key issue in the fabrication of optical based glass for solid state lasers and light emitting devices. Hence, we report the Nd^{3+} concentration dependent on optical parameters such as absorption edge, optical band gap (direct and indirect) and Urbach's energy of gadolinium borophospho-tellurite glasses with chemical composition of $10Gd_2O + 30B_2O_3 + 20P_2O_5 + (40\text{-}x)TeO2 + xNd_2O_3$ (where $0.0 \leq x \leq 1.0$ mol%). The glass samples were synthesized by convectional melt quenching method and characterized through X-Ray Diffraction (XRD) and Ultraviolet Visible Near-Infrared (UV-Vis-NIR) measurements. The amorphous nature of these glasses was confirmed by X-Ray diffraction pattern while the UV-Vis-NIR spectra revealed six absorption peaks corresponding to the transition from ground level $^4I_{9/2}$ to the various excited state of Nd^{3+} ions. It was found that the investigated range of Nd^{3+} doping concentrations has a great influence on aforementioned parameters. The excellent optical features established in the present glass host suggest their potentiality for solid-state lasers and other photonic applications.

Keywords: a*bsorption spectra, borophospho-tellurite glasses, Neodymium ions, optical band gap and Urbach's energy*

INTRODUCTION

Driven by the quest for practical and efficient solid-state lasers, neodymium (Nd^{3+}) doped glasses have captured the attention of esteem material scientists, physicists, physical chemists and engineers in the search of novel glass hosts with optimized optical properties.

Recently, passionate efforts have been focused on the synthesis and characterization of multi-component oxide glasses such as borophosphate (Marimuthu, 2016), sulfoborate (Dalhatu *et al.*, 2016), borosulfophosphate (Kumar *et al.*, 2012), borotellurite (Lakshminarayana *et al.*, 2017) and borosilicate (Rao *et al.*, 2014) glasses for various scientific and technological applications. Among the convectional multi-component glass families, borophospho-tellurite glass host has been chosen in this study because combination of B_2O_3, P_2O_5 and Te_2O_3 will enhance not only the physical and electrical properties but also the UV and IR transmission abilities (Maheshvaran and Marimuthu, 2012, Gomes *et al.*, 2017). In addition, the presence of tellurite in a glass matrix containing B_2O_3 and P_2O_5 will decrease its hydroscopic nature which is of scientific and practical interest (Selvi *et al.*, 2016).

Furthermore, borophospho-tellurite glass host represents favorable compromise between the requirements of low phonon energy, cost effective properties, a relatively high thermal stability and high chemical durability (Selvi *et al.*, 2015). Addition of Gd_2O into borophospho-tellurite glass network produces low rates of crystallization and increases the glass forming ability.

Despite the promising features of these glasses, tailoring the optical parameters such as absorption edge, optical band gaps and Urbach's energy of rare earth doped borophospho-tellurite glasses which is the key issue to attain high quality optical systems is not fully understood. However, the effect of Nd^{3+} on the optical properties of gadolinium borophospho-tellurite glasses to the best of our knowledge has not been studied in any great detail. Motivated by these considerations, we have prepared godilinium borophospho-tellurite glass doped with Nd^{3+} ions and, examined the influence of varying concentration of Nd^{3+} on the optical properties.

EXPERIMENTAL PROCEDURE

SAMPLE PREPARATION

High purity analytical grade (from Sigma Aldrich, 99.99% purity) such as godilinium carbonate (Gd_2CO_3), boric acid (H_3BO_3), phosphoric acid (H_3PO_4) and Neodymium oxide (Nd_2O_3) have been used to synthesize Nd^{3+} doped godilinium-borophospho-tellurite glasses following normal melt quenching procedure.

Each batch composition of about 20 g were weighted via precision balance and thoroughly mixed in porcelain crucible to obtain a homogenous mixture. The achieved mixture was taken into an electrical furnace for sintering. Herein, two sintering process was employed. Firstly, the homogeneous mixture of the samples was pre-heated at 400°C for 45 min to facilitate the vaporisation of water (H_2O) and carbon dioxide (CO_2). Secondly, the samples were melted by increasing the furnace temperature to 1000°C and maintained for 1hr until the mixture became molten and homogeneous. The resultant bubble free melt was then poured on the preheated brass plate kept in another furnace and annealed at 350 °C for 4hr in order to remove the internal strains, cracks and to improve the mechanical strength of the prepared glasses. Upon completing the annealing process, the furnace was gradually cooled down to room

temperature. Finally, the prepared glass samples were well polished on both sides before further optical measurements. The details chemical composition of the present glass system is presented in Table 1.

Table 1: Detail chemical composition of godilinium borophospho-tellurite glasses doped with different concentration of Nd^{+3} ions (in mol %)

S/no	Sample code	Gd_2O	BO_3	P_2O_5	TeO2	Nd_2O_3
1	0.05Nd	10	30	20	39.95	0.05
2	0.1Nd	10	30	20	39.9	0.1
3	0.5Nd	10	30	20	39.5	0.5
4	1.0Nd	10	30	20	39.0	1.0

CHARACTERIZATION AND MEASUREMENT

X-RAY DIFFRACTION (XRD) MEASUREMENT

In this study, the X-Ray diffractograms of the powder samples were recorded at room temperature via Siemens X-Ray Diffractometer D5000 with Cukα (λ=1.54Å) having the power source of 40kV and 30mA, and 2θ was varied from 10° to 80° at scanning rate of 2° per minute to ascertain the amorphous nature of the synthesized samples.

UV-VIS-NIR MEASUREMENT

The optical absorption spectra for all Nd^{3+}-doped samples were obtained at room temperature using Shimadzu 3101 UV-Vis-NIR spectrophotometer in the range of 200 – 2400 nm

THEORETICAL APPROACH

FUNDAMENTAL ABSORPTION EDGE AND OPTICAL BAND GAP

Absorption edge study in UV region is a useful method to understand the optical transition and electronic band structure in glasses. Mott and Davis proposed the relation between absorption coefficient and photon energy to calculate indirect and direct transitions occurring in a band gap.

The photon energy can be calculated by using the following equation (Jlassi *et al.,* 2016):

$$\hbar\omega = \frac{h}{2\pi}(2\pi f) = \frac{h}{c\lambda} \quad (1)$$

Where: *c=2.9979X108 (m/s) and ħ=4.14 X* 10^{-15} *(eVs)*

Following the Mott and Davis relation given by (Mhareb *et al.,* 2014):

$$\alpha(\omega) = \frac{A(\hbar\omega - E_{opt})^n}{\hbar\omega} \quad (2)$$

The direct and indirect optical transition can be calculated from the plot of absorption coefficient α (ω) as a function of photon energy ħω.

Where A is a constant related to the extent of the band tailing. n=1/2 for direct allowed transition and n= 2 for indirect transitions. Eopt is the optical energy gap between the valence band and the conduction band.

URBACH'S ENERGY (ΔE)

The Urbach energy, ΔE is defined as the energy gap between localized tail states in the forbidden band gap. It provides a measure of disorder in the amorphous and crystalline solids. In amorphous materials, structural disorder dominates and this could be due to the presence of structural defects like dangling bonds or non-bridging oxygen atoms

The absorption coefficient at the photon energy below optical band gap (tail absorption) depends exponentially on the photon energy and obeys empirical relation given by (Obayes *et al.,* 2016):

$$\alpha(\omega) = C\exp(\frac{\hbar\omega}{\Delta E}) \quad (3)$$

The above equation can further be expressed as:

$$\ln\alpha = \frac{\hbar\omega}{\Delta E} + C \quad (4)$$

From equation 4 above, the value of ΔE is estimated by taking the inverse of the slope from the plot of $\ln\alpha$ versus ħω. Where *C*, represent a constant (Intercept)

RESULTS AND DISCUSSION

X-RAY DIFFRACTION (XRD) STUDIES

Figure 1 depicted the x-ray diffraction pattern for the prepared glass samples. From Figure 1, the presence of a broad hump in the range of 5 – 30 degree indicates that the fabricated samples do not have long range periodic lattice arrangement. However, the absence of sharp lines and peaks revealed that the samples are amorphous in nature. Since glasses do not have uniformly spaced planes of atoms, therefore no sharp diffraction pattern will be observed in the diffraction pattern.

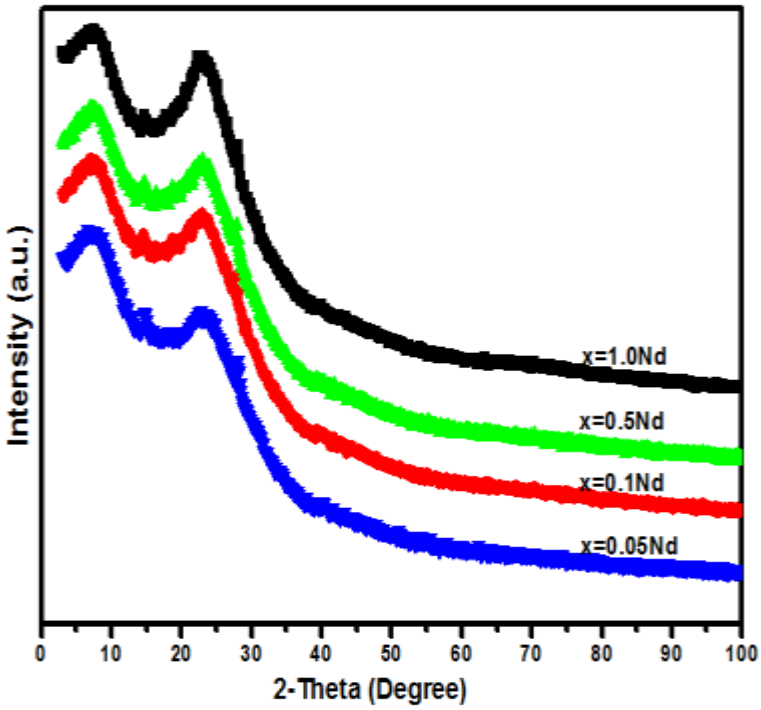

Figure 1: XRD pattern of Gd_2O-B_2O_3 -P_2O_5-TeO2 glasses doped with different concentration of Nd^{+3} ions

OPTICAL ABSORPTION, ENERGY BAND GAP AND URBACH'S ENERGY STUDIES

The study of the optical absorption is significant because it gives basic information about the optically induced transitions, band structure, and energy gap of a material. For a crystalline material, the absorption edge will be very sharp whereas in an amorphous material the fundamental absorption edge will has a finite slope.

Figure 2 demonstrates the UV-VIS-NIR absorption spectra of the glass samples in the wavelength range of 400 – 1000 nm with the various spectroscopic transitions from the ground state $^4I_{9/2}$ to the excited states $^2K_{15/2}$ (470 nm), $^4G_{7/2}$ (523 nm), $^2G_{5/2}$ + $^2G_{7/2}$ (580 nm), $^4S_{3/2}$ + $^2F_{7/2}$ (743 nm), $^4F_{5/2}$ + $^2H_{9/2}$ (804 nm) and $^4F_{3/2}$ (878 nm), respectively. It is observed from the Figure that, the absorption bands increase proportionality with Nd_2O_3 concentration

However, the absence of sharp absorption edges as shown in Figure 2 further reaffirm XRD result, confirming that the present samples are fully amorphous in nature.

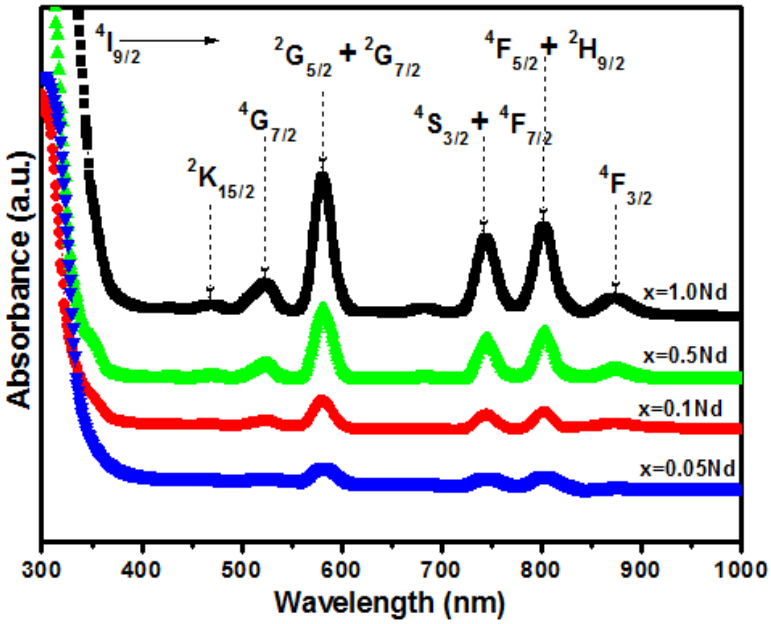

Figure 2: Optical absorption spectra of Gd_2O-B_2O_3-P_2O_5-TeO_2 glasses doped with different concentration of Nd^{+3} ions**.**

From the absorption spectra (Figure 2), a plot of $(\alpha\hbar\omega)^2$ versus $(\hbar\omega)$ and $(\alpha\hbar\omega)^{1/2}$ versus $(\hbar\omega)$ are made and presented in Figure 3 and 4 respectively. The values of direct(E_{opt}^1) and indirect(E_{opt}^2) optical energy band gaps are estimated by extrapolating the linear part of these plots. Hence the point of intersection on the horizontal axis $(\hbar\omega)$ gives the energy band gap of the sample. These values are summarized in Table 2. It can be seen that the value of the optical band gaps, direct and indirect are in the range of 2.476 – 2.078 and 2.304 – 1.529 eV, respectively close to the values obtained by previous researchers (Nurhafizah *et al.*, 2016, Rao *et al.*, 2014). Furthermore, it is observed that the optical band gaps (both direct and indirect) decreases with the increase in Nd^{3+} content. This decrement is associated with the structural changes occurring in the prepared glass. Conversely, the increase in Nd^{3+} contents may enhance the degree of localization by creating defect in the charge distribution and drive the energy levels of the closet oxygen ions nearer to the top of the valence band and thereby raise donor centers in the glass matrix. These increase in donor centers lead to a decrease in energy band gap.

Table 2: Cut-off wavelength, optical band gaps and urbach energy values of Gd_2O-B_2O_3-P_2O_5-TeO2 glasses doped with different concentration of Nd^{+3} ions

Samples	Cutt-off wavelength, λ (nm)	Direct band gap, E_{opt}^1 (eV)	Indirect band gap, E_{opt}^2 (eV)	Urbach's energy, ΔE (eV)
0.05Nd	350	2.476	2.303	0.176
0.1Nd	358	2.374	2.149	0.279
0.5Nd	360	2.306	1.767	0.352
1.0Nd	373	2.078	1.529	0.372

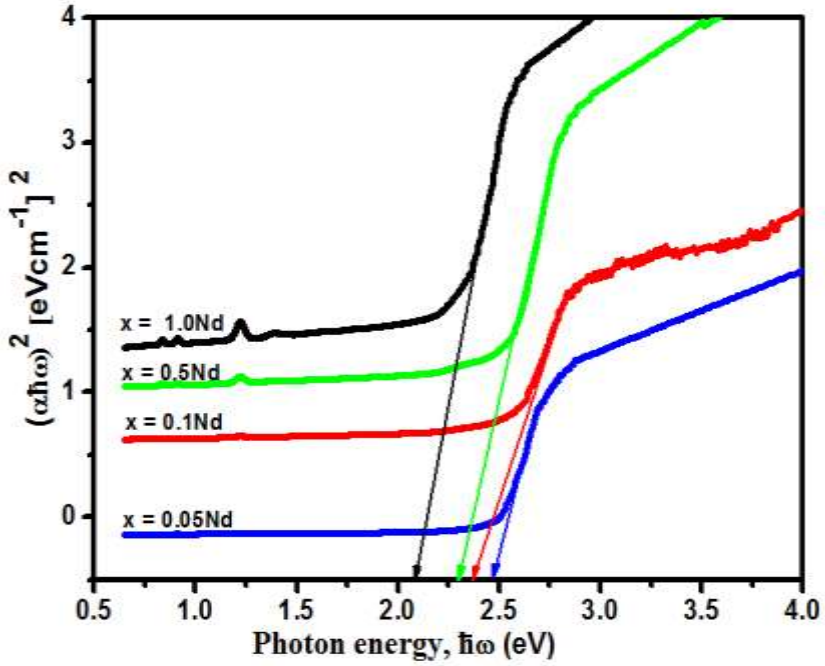

Figure 3: Direct optical energy band gap of Gd_2O-B_2O_3 -P_2O_5-TeO2 glasses doped with different concentration of Nd^{+3} ions

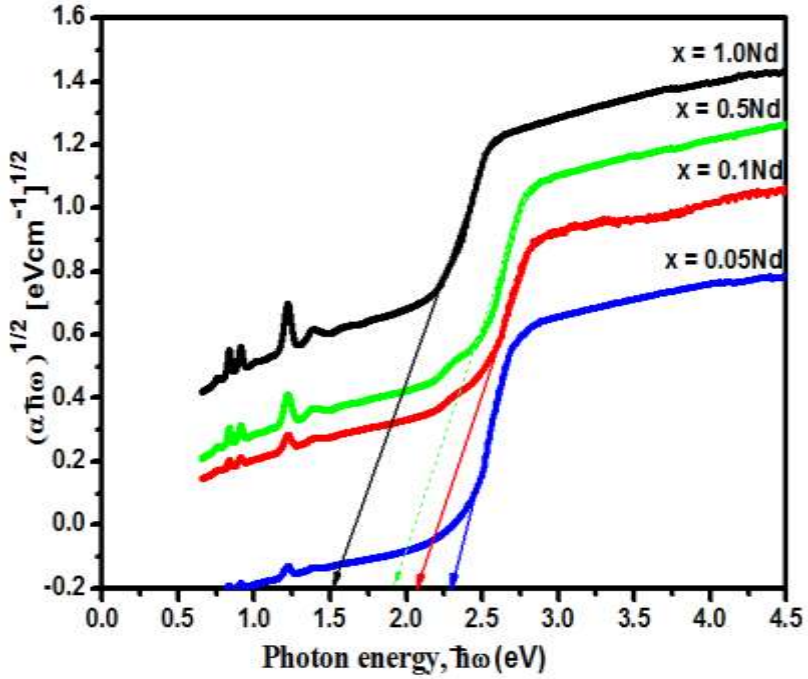

Figure 4: Indirect optical energy band gap of Gd_2O-B_2O_3 -P_2O_5-TeO2 glasses doped with different concentration of Nd^{+3} ions.

Figure 5 depicted the Urbach energy plots of the samples studied. The values of Urbach energy calculated from the inverse slope are found to lie between 0.312–0.316 eV as presented in Table 2. The observed increase in

Urbach energy with the increase of Nd^{3+} concentration is due to the formation of bonding defects and non-bridging oxygen. These values are well within the range of 0.046–0.66 eV for amorphous semiconductors (Medhat *et al.*, 2017). Generally, Urbach's energy values vary inversely with optical band gap values. The lower values of Urbach's energy indicate that prepared glass sample possess minimum defects and less disorderliness which in turn leads to structural rearrangement.

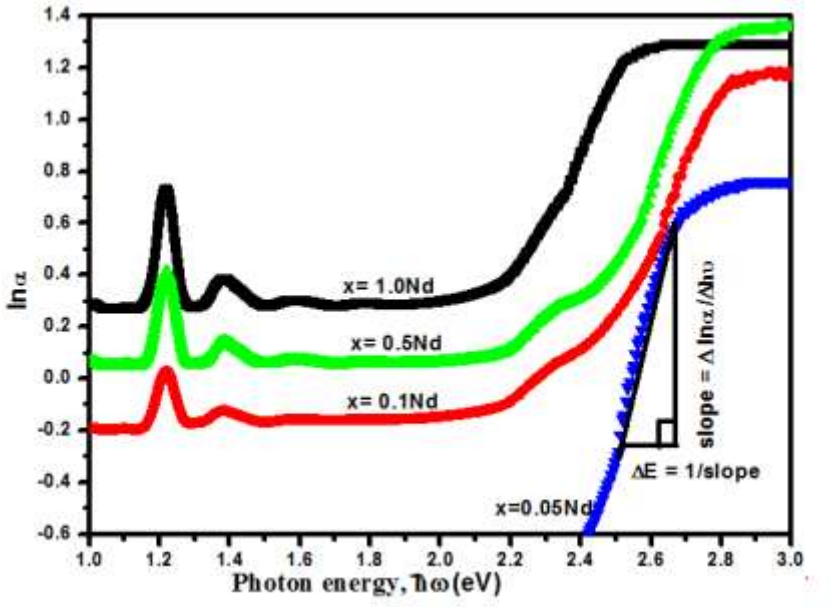

Figure 5: Urbach's energy plot of Gd_2O-B_2O_3-P_2O_5-TeO2 glasses doped with different concentration of Nd^{+3} ions

CONCLUSIONS

The effect of neodymium oxide ions on the optical properties of gadolimium borophospho-tellurite glasses synthesized through melt quenching technique has been investigated using X-Ray Diffraction and optical absorption measurements. The XRD pattern verified the amorphous nature of the prepared samples whereas the fundamental absorption edge (cut-off wavelength), optical energy band gap (both direct and indirect) as well as the urbach's energy deduced from the absorption spectra are strongly influenced by the variation of Nd_2O_3 concentration. The optical absorption spectra which contain six absorption bands exhibit a significant peak at 580 nm for 1.0Nd sample. This promising feature suggest that the present glass sample containing 1.0 mol% of Nd^{3+} could contribute towards the development of borophosho-tellurite glass based lasing devices.

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