

OPTICAL CHARACTERIZATION OF Nd³⁺ DOPED TeO₂-ZnCl₂

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ABSTRACT

Understanding optical properties of tellurite glasses modified and fabricated by controlling Nd³⁺ doping are promising for photonic applications. Neodymium doped zinc-tellurite glasses of composition (70-x)TeO₂-30ZnCl₂-xNd₂O₃ with concentration from 0.0 to 3.0 mol% (x=0, 1, 2 and 3) were prepared by using an ordinary melt-quench casting technique. The amorphous nature of the glass were confirmed from x-ray diffraction technique. The UV absorption spectra recorded nine bands and the values of the indirect optical band gaps found between 2.76-3.20 eV, while the Urbach energy values varies are between 1.20-2.59 eV. The indirect optical energy gap for indirect transition and Urbach energy had minimum value for Nd³⁺ at 1% mol. The varying concentration of Nd³⁺ ions found to have a strong effects on optical and structural properties of the glass.

Keywords: Tellurite glass; Neodymium; optical; Optical band gap;

INTRODUCTION

Rare earth (RE) elements doped materials had a great consideration due to their numerous photonic applications and techniques as solid color displays, state lasers, up-conversion lasers, optical telecommunication, optical fiber amplifiers, optical data storage etc.,[1]. Therefore, Nd³⁺ doped tellurite glasses proved to be one of the most powerful candidates for photonic devices and its applications[2]. Tellurite has got an attention due to it is high rare-earth ion solubility, low phonon energy (~780cm⁻¹), low melting temperature (less than 1100°C, and high refractive index (~2.0) and possess a good thermal and chemical stability. Therefore, tellurite are the advisable candidates for various longer wavelength applications [2-4]. Research and studies in the optical characteristics of Nd³⁺ ions in the UV region is still controversial. The objectives of this study to examine the role of Nd³⁺ ions on the optical characterizations as indirect optical band gap and Urbach energy of the tellurite glass.

EXPERIMENTAL

The tellurite glass of (70-x) TeO₂-30ZnCl₂-xNd₂O₃ glasses system is prepared where (x= 0, 1, 2 and 3) by using melt-quenching technique. Batches of 15g were prepared from certified reagent grades of TeO₂ (≥99% purity is from Sigma-Aldrich (Japan)), ZnCl₂ (99.99% purity is from Merck (Germany)) and Nd₂O₃ (99.99% purity is from Sigma-Aldrich (USA)) designated as TZN0, TZN1, TZN2 and TZN3 respectively. Firstly, chemical compounds mixed in a platinum crucible (30ml) and heated at 900°C (furnace from Nabertherm GmbH/1600°C-8.0kW-400Volt) for 30min. After the batch is completely melted, the melts cast onto the preheated stainless steel plate followed by annealing at 250°C for 5 h before allowed to cool down to room temperature. The prepared samples grain by using different degree of sandpaper with different micro-grits (P240 and 400) then polished (using Diamond compound -Hyprez five star –gauges: 1-FS-47, 3-FS-47 and 6-FS-47) until the appropriate thickness (1.3-3) mm achieved with high transparency. The structural characterizations are made by x-ray diffraction (Siemens D5000 X-Ray Diffractometer). The room temperature optical absorption of the samples is measured in the wavelength range 200-1800 nm by UV-VIS-NIR scanning spectrophotometer (UV-3101PC). The optical absorption coefficient $\alpha(\lambda)$ were calculated using Beer-Lamber equation:

$$\alpha(\lambda) = 2.303 \frac{A}{d} \quad (1)$$

where A is absorbance and d is the sample thickness.

RESULT AND DISCUSSION

Figure 1 shows the broad peak (centered in 28.5°) called *as halo* in the XRD patterns of samples to confirm the amorphous in nature of the glasses.

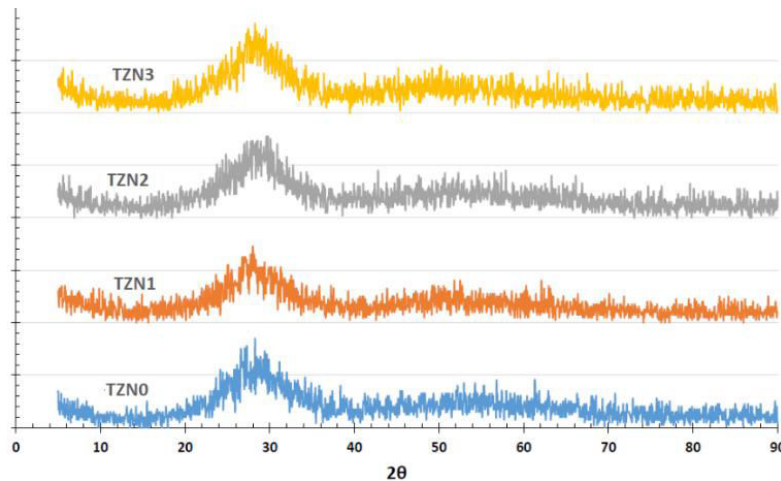


Figure 1: XRD patterns of the Nd³⁺ doped TZN glass samples

Figure 2 shows the optical absorption spectra of the glasses consists of nine broaden band corresponded to 4f-4f transition of Nd^{3+} ions[5].

Nine absorption bands with different relative intensities have been observed correspond to Nd^{3+} transitions from ground state of $^4\text{I}_{9/2}$ to the excited state of $^4\text{F}_{3/2}$ (875nm), $^4\text{F}_{5/2}$ (804nm), $^4\text{F}_{7/2}$ (747nm), $^2\text{H}_{9/2}$ (683nm), $^4\text{H}_{11/2}$ (630nm), $^4\text{G}_{5/2}$ (585nm), $^4\text{G}_{7/2}$ (522nm), $^4\text{G}_{9/2}$ (471nm) and $^4\text{P}_{1/2}$ (428nm). The values of absorption bands are in a good agreement with Prnova *et al.*[6], Dan *et al.*[5], Ramteke *et al.*[7] and Rumnikhom *et al.*[8].

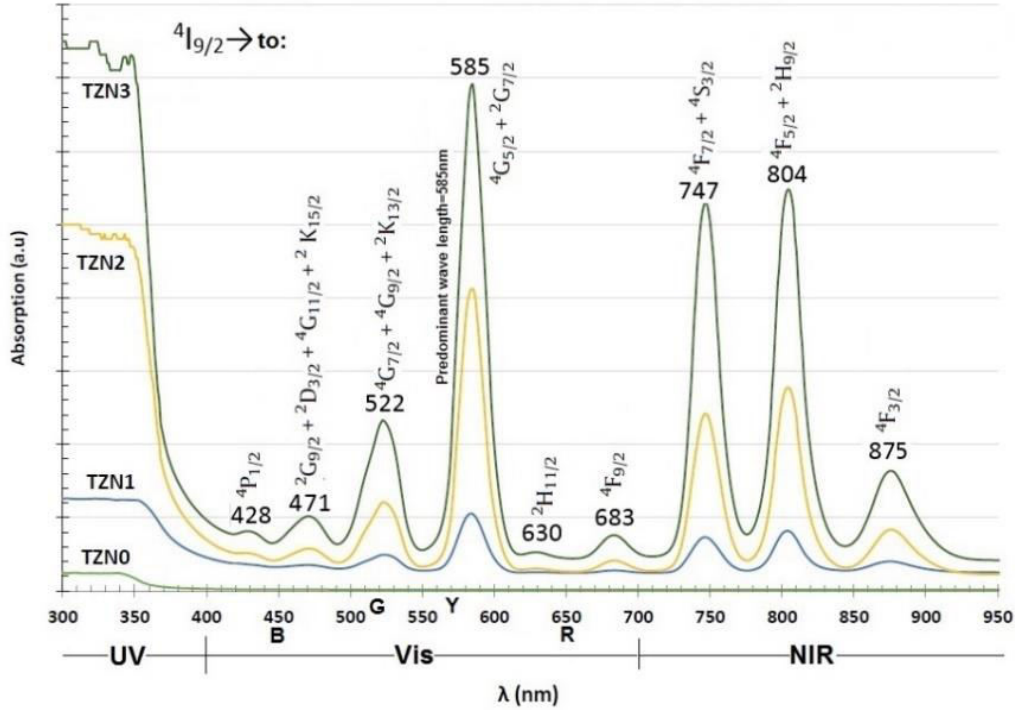


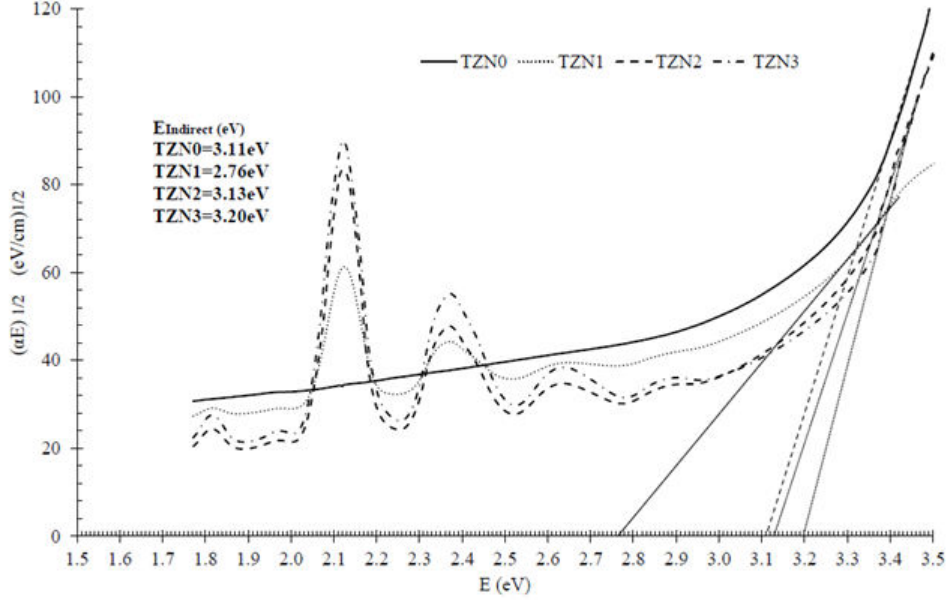
Figure 2: Optical absorption spectra of glasses with different mol % of Nd_2O_3

From Tauc equation (Eq. 2) which been developed by Matt and Davies[9], the fundamental absorption edges of absorption spectra calculated to investigate optical transitions in amorphous materials that involves interaction of photon with electron in valence band to access information about the energy band gap and structures of glass sample. The conduction band and the plotting data of optical energy band gap shows in Figure 3 (a) which obtained by transforming extrapolation data to linearized data[9, 10].

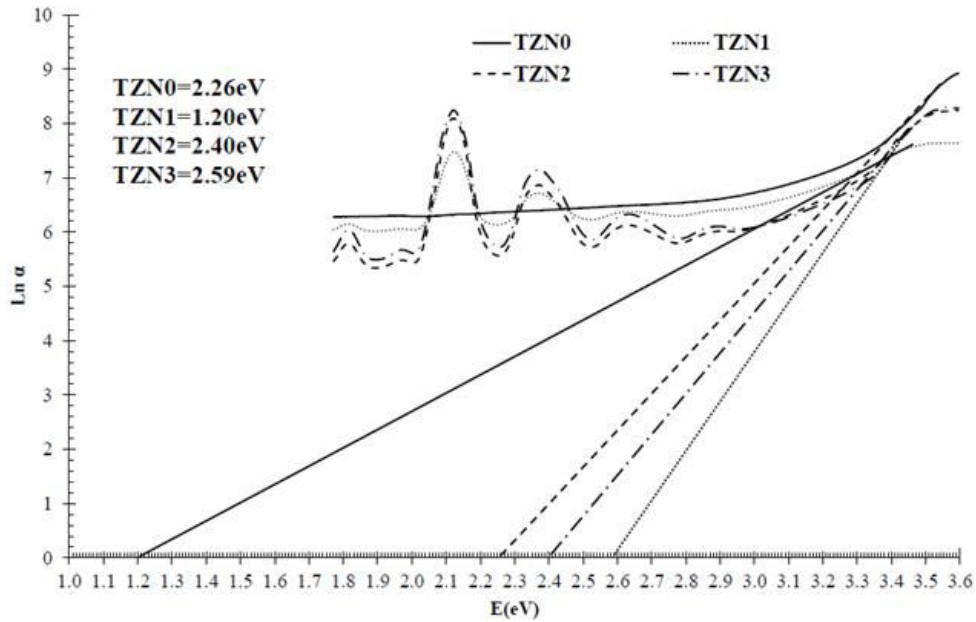
$$\alpha(\omega) = \text{const.} \frac{(\hbar\omega - E_{\text{opt}})^2}{\hbar\omega} \quad (2)$$

where, E_g is the energy of the optical band gap and $\hbar\omega$ is the photon energy. The value $n=2$ is for indirect transitions. From Eq. 2, it is found that best reasonable fit for most amorphous material is at $n=2$, representing the indirect allowed band transition and it is the most dominate transition[6]. The interactions of photons with lattice vibrations at this allowed indirect transition will take place. The value of E_g can be obtained by

extrapolating the linear part of the $(\alpha\hbar\omega)^{1/2}$ versus phonon energy, $\hbar\omega$ graph to the axis shown in Figure 3(a). The optical gap is obtained from the intersection of this line with the energy axis[9]. The indirect optical band gap was found to vary from 2.76-3.20 eV as increasing the content of Nd_2O_3 and it looks linear for high absorption coefficient, but tend to be constant at low photon energy[10, 11].



(a)



(b)

Figure 3: (a) Plot of $(\alpha E)^{1/2}$ versus photon energy E for indirect band gap and (b) Plot of $(\ln \alpha)$ versus E for Urbach energy of $(70-x)\text{TeO}_2-30\text{ZnCl}_2-x\text{Nd}_2\text{O}_3$ glass system

In amorphous material, the $\alpha(\omega)$ depends exponentially on the $(\hbar\omega)$ which is known as the Urbach rule as expressed in Eq. 3:

$$\alpha(\omega) = B e^{\Delta E_g / \hbar\omega} \quad (3)$$

where, B is a constant and ΔE is the width of the band tail of the electron states. From Figure 2(b), Urbach energy is calculated from the slope of plot $\ln(\alpha)$ versus $\hbar\omega$. The values of Urbach energy found to lie between 1.20-2.59 eV for glass system. The values for indirect optical band gap and Urbach energy are presented in table 1.

Table 1: Indirect optical band gap, E_g and Urbach energy, ΔE of $(70-x)\text{TeO}_2$ - 30ZnCl_2 - $x\text{Nd}_2\text{O}_3$ glass system.

Glass samples	Mol fraction (mol%)			Indirect optical band gap E_g (eV)	Urbach energy ΔE (eV)
	TeO_2	ZnCl_2	Nd_2O_3		
TZN0 (Undoped)	70	30	0	3.11	2.26
TZN1	69	30	1	2.76	1.20
TZN2	68	30	2	3.13	2.40
TZN3	67	30	3	3.20	2.59

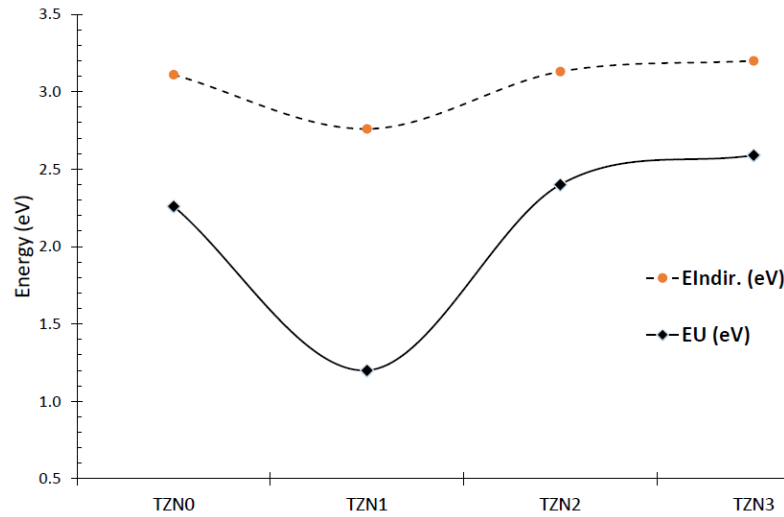


Figure 3: The optical band gap energy, E_g and Urbach energy, ΔE of $(70-x)\text{TeO}_2$ - 30ZnCl_2 - $x\text{Nd}_2\text{O}_3$ glass system for $x=0, 1, 2$ and 3

Figure 3 shows that the optical band gap energy, E_g and Urbach energy have minimum value with Nd^{3+} at 1mol%. This observation is attributed to the formation of non-bridging oxygen (NBO) which reduce the glass's band gap due to the increasing static disorder and widening the energy band gap between conduction and valence states[12].

CONCLUSION

A glasses series of $\text{TeO}_2\text{-ZnCl}_2\text{-Nd}_2\text{O}_3$ with different Nd_2O_3 concentration has prepared by melt-quenching technique and the glass amorphous nature proved by XRD. The optical absorption in UV-VIS-NIR has been investigated. The optical absorption spectra in the range of 300-950 nm used to calculate optical band gap (2.76-3.20)eV and Urbach energy (1.20-2.59) eV. It was found that the optical energy gap for indirect forbidden transition and Urbach energy have minimum value at 1mol% of Nd^{3+} concentration and it depend on the non-bridging oxygen in the glass system. The role of Nd^{3+} ions in modifying the optical energy gap been understood. The results are considerable and may participate to develop rare earth doped tellurite glasses for solid state lasers and sensors. It is important to look for more investigation by using Photoluminescence, FTIR and Raman spectra.

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