# Preparation and characterization of $Nd^{3+}/Er^{3+}$ ions co-doped zinc-tellurite glass system

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***Abstract*—Neodymium/Erbium ions co-doped in the system of zinc-tellurite with the composition of (70-2x)$TeO_2$-30$ZnCl_2$-x$Nd_2O_3$-x$Er_2O_3$ concentration from 1.0 to 3.0 mol% (x=1, 2 and 3) glasses were prepared by using conventional melt-quenching technique. The amorphous nature of the glass was confirmed from x-ray diffraction technique. The UV absorption spectra recorded several bands and the values of the optical band gaps found around 3eV, while the Urbach energy values varies are between 0.27-1.01 eV. The optical energy gap for indirect transition and Urbach energy had minimum value for $Nd^{3+}/Er^{3+}$ at 1% mol. The varying concentration of $Nd^{3+}$ and $Er^{3+}$ ions found to have a strong effects on optical and structural properties of the glass.**

*Keywords: Tellurite glass, Neodymium and Erbium ions, co-doping, characterization.*

## I. INTRODUCTION

The glasses based on tellurium oxide ($TeO_2$) are exploited as glass hosts due to their new optical characteristics with varieties of applications. $TeO_2$ is a promising industrial material as optical amplifiers [1]. In addition, it also shows interesting properties in the structure and glass forming ability. In $TeO_2$ structures, the coordination circumstance of Te changes from $TeO_4$ to $TeO_3$ upon the additional of alkaline dopants or the raising of the temperature [2].

Dandan *et al.* [3] recently reported that one chalcogen (Te) element could significantly enhanced the transmission capability, moisture resistance and transparency in the mid-infrared (at around 3 μm) band lasers regions for their use as optical materials with suitable dopant rare earth ions. The glasses doped or co-doped with rare-earth ions have generated much interest due to the possibility of several promising applications such as optical data storage, visible laser, fiber amplifier, optical communication and sensor devices [4, 5].

However, the high concentration of dopant quenches the performance of amplifiers and laser. Improving the up-conversion emission and the quantum efficiency are the key issue [1, 6]. A lake studies exist in the literatures on the characteristics of tellurite glass co-doped with $Er_2O_3$ and $Nd_2O_3$. The mechanism behind the concentration quenching is still debatable. In view of the above, it has to examine the role of co-doping on thermal and optical properties of tellurite glasses. In this work, spectroscopic techniques employed to investigate the optical properties of $Er^{3+}/Nd^{3+}$ co-doped tellurite glass system.

## II. Experimental Details

The glass samples were prepared by singing rapid melt quenching technique. The series of three binary glass system (coded as TZNE1, TZNE2 and TZNE3) consist of $(70\text{-}2x)TeO_2\text{-}30ZnCl_2\text{-}xNd_2O_3\text{-}xEr_2O_3$ with x = 1.0 to 3.0 mol % are shown in Table 1. A homogenized material batches of 10 g components were placed in a platinum crucible and being melted in a furnace (furnace from Nabertherm GmbH/1600ºC-8.0kW-400Volt) at 900ºC for 0.5 hours. After the required viscosity was achieved the melt were then coated on a metal plate and annealed at 260 º C for 3 hours. Finally, the temperature of the samples cooled down inside the furnace to room temperature for 12 hours.

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).

## III. RESULTS AND DESCUSION

The measured and calculated values of the optical band gaps and the Urbach energy for $Er^{3+}/Nd^{3+}$ co-doped tellurite glasses are listed in Table 1.

**Table 1. Optical parameters of $Er^{3+}/Nd^{3+}$ co-doped tellurite glass.**

| *Glass sample* | *Mol fraction (mol %)* | | | | *Optical band gap $E_{opt}$ (eV)* | *Urbach energy, ΔE (eV)* |
|---|---|---|---|---|---|---|
| | *$Er_2O_3$* | *$Nd_2O_3$* | *$TeO_2$* | *$ZnCl_2$* | | |
| **TZNE1** | 1 | 1 | 68 | 30 | 3.07 | 1.29 |
| **TZNE2** | 2 | 2 | 66 | 30 | 3.03 | 1.37 |
| **TZNE3** | 3 | 3 | 64 | 30 | 3.02 | 1.36 |

To check the amorphous state of the glass samples, X-ray measurements were performed. The short and medium-range orders in the binary system consist of $(70\text{-}2x)TeO_2\text{-}30ZnCl_2\text{-}xNd_2O_3\text{-}xEr_2O_3$ glass system structures were tested by means of X-Ray diffraction. The diffraction patterns (Fig. 1) of all powder glass samples showed broad humps over the region 20-35º for $2\Theta$ values, which confirm the amorphous in nature of the glasses [7].

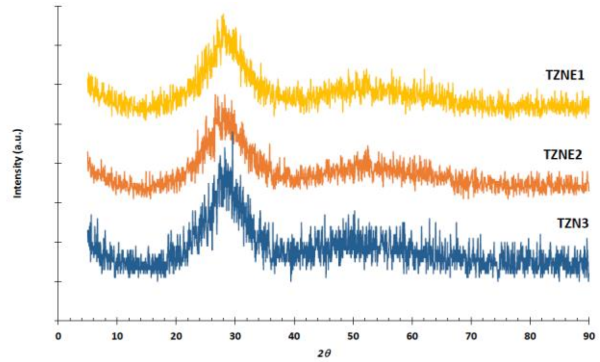



Fig 1. XRD patterns of $(70\text{-}2x)TeO_2\text{-}30ZnCl_2\text{-}xNd_2O_3\text{-}xEr_2O_3$ glasses.

The study of absorption edge in the UV region supply useful information towards the investigation of optical induced transitions, optical band gaps and electronic band structures in crystalline and amorphous materials. The principle based on the absorption of a photon with energy greater than the band gap energy. Direct and indirect optical transition can occur at the fundamental absorption edge. Both the optical transition involved in the interaction of an electromagnetic wave with an electron in the valence band. Fig. 2 shows the typical absorption spectrum of $Er^{3+}/Nd^{3+}$ co-doped tellurite glasses.

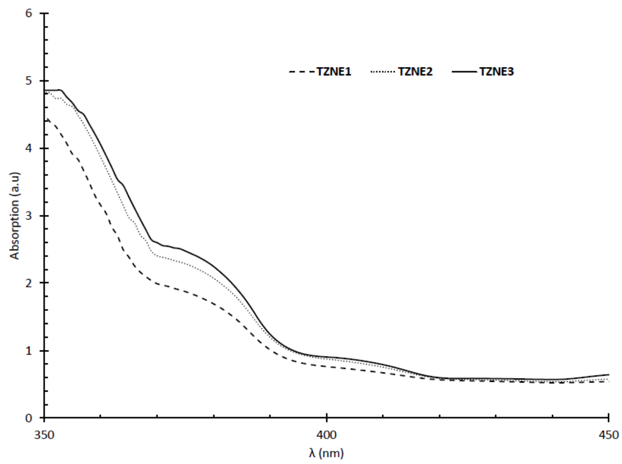


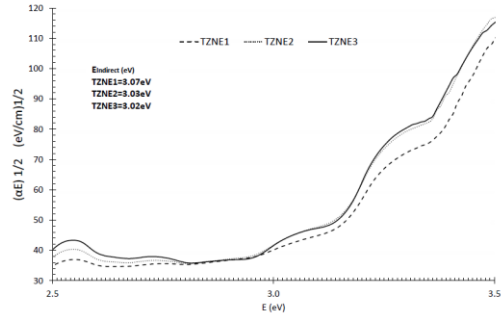

Fig 2. Variation of absorption coefficient with wavelength for different $Nd^{3+}/Er^{3+}$ mol%.

The absorption coefficient α (ω) in amorphous materials is given by Davis and Mott as a function of photon energy (ħω) for the direct and the indirect transition [8].

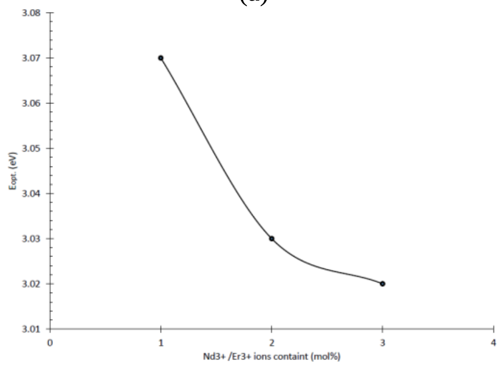
The relation between α (ω) and photon energy of the incident radiation can be written as [9, 10]:

$$\alpha(\omega) = const.\frac{(\hbar\omega - E_{opt.})^n}{\hbar\omega} \quad (1)$$

where α (ω) is the absorption coefficient at an angular frequency ω, ħ is the Planck constant divided by 2π and *n* is an index depending on the nature of the electronic transition responsible for the absorption. The values of $n$ is 1/2 (for allowed direct transitions), 3/2 (for direct forbidden transitions), 2 (for allowed indirect transitions) and 3 (for forbidden indirect transitions). From (1), the values of $E_{opt}$ are determined by extrapolating linear a region of the plot $(\alpha\hbar\omega)^{1/2}$ against ħω to $(\alpha\hbar\omega)^{1/2}=0$ for all three samples as shown in Fig. 3(a).




(a)




(b)

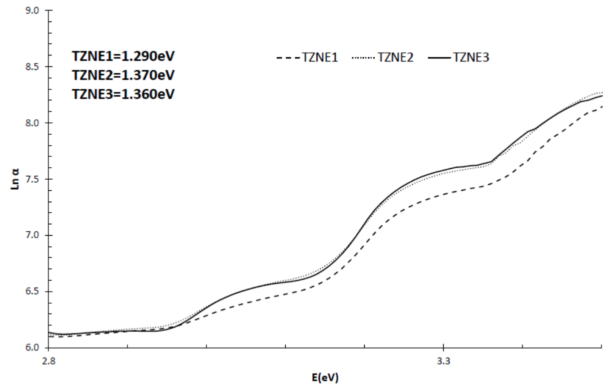
Fig 3. (a) A plot of $(\alpha\hbar\omega)^{½}$ versus photon energy (ħω) for all the samples and (b) A plot of Optical band gap ($E_{opt.}$) against $Nd^{3+}/Er^{3+}$ content (mol %)

The variation of the optical energy band gap ($E_{opt}$) vs mol% of $Er_2O_3$ is shown in Fig. 3(b), following Table 1. Fig. 3(b) clearly shows the gradually decreasing of the optical band gap as the $Nd^{3+}/Er^{3+}$ content is increased (decreasing $TeO_2$ and increasing rare earth ions). These values were less than the ternary tellurite glass [11]. This result shows that the covalent nature of the glass matrix decrease with low concentration of rare earth ions and $TeO_2$ [12].

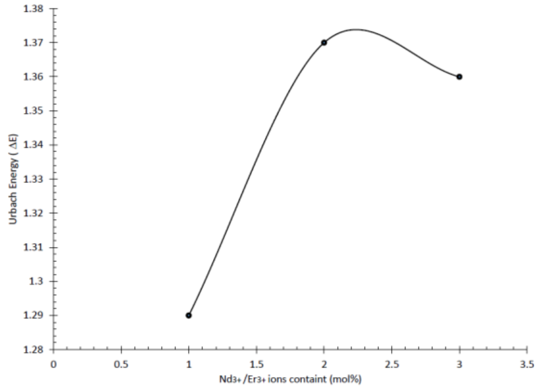
Fig. 4(a) shows the variation of ln(α) with the photon energy. The values of Urbach energy are calculated by determining slopes of the linear regions of the curves at lower photon energies and taking their reciprocals corresponding to the expression given by [7, 13],

$$\ln \alpha(\omega) = \frac{\hbar\omega}{\Delta E} - C \qquad (2)$$

where $C$ is a constant and $\Delta E$ is the Urbach energy.




(a)




(b)

Figure 4: (a) A plot of lnα against photon energy, ħω and (b) plot of Urbach Energy, ΔE against $Nd^{3+}/Er^{3+}$ content (mol %).

The value of Urbach energy was between 1.29eV and 1.37eV (Table 1). A plot ΔE against $Nd^{3+}/Er^{3+}$ mol% content presented to examine the clear nature of the optical gap in Fig. 4(b). It can be seen from the figure that the Urbach Energy have a maximum value for the concentration of the sample TZNE2. Meanwhile, the much lower value of Urbach energies observed for the TZNE1 and TZNE3 presented glasses which suggests that the defects in these glasses are minimum [12]. The results are in good agreement with previous report in which the addition of rare-earth to the oxide glass shows a reduction in optical band gaps as well as Urbach energies with the densification of the glass network [12]. The lowest values Urbach Energy (ΔE=1.29 eV) was observed for the TZNE1 glass. The estimated optical energy gap, $E_{opt}$ at the fundamental absorption edge is smaller in the doped glass as compare to the host glass. This condition has also proposed related to the creation of higher number of NBOs units after the incorporation of both $Er^{3+}$ and $Nd^{3+}$ ions into the host matrix. In general this phenomenon is related to the oxygen bond strength in the glass network [14] and it is expected that electrons are less tightly bounded, hence caused the reduction of the $E_{opt}$ value [15]. The obtained optical energy gap values of the studied glasses are in a good agreement with the range of the values in various tellurite glasses reported by [11, 16, 17].

## IV. CONCLUSION

The role of co-doping on optical of tellurite glasses with composition (70-2x)$TeO_2$-30$ZnCl_2$-x$Nd_2O_3$-x$Er_2O_3$ (x = 1.0 to 3.0 mol%) were investigated. The amorphous nature of the prepared samples by melt-quenching method is confirmed by XRD. The Optical absorption behavior is measured using UV-VIS-NIR spectroscopy. It was observed that the values of optical band gap are increased but the values of Urbach energy is variates with increasing of $Nd^{3+}$/$Er^{3+}$ contents with decreasing of $TeO_2$. The permutation of the Urbach energy shows the compactness of the glassy network. Both the optical band gap and the Urbach energy are found to be a strong function of the dopant concentration. The results are in good agreement with other researchers work. The glass forming mechanism is understood. It is interesting to investigate the photoluminescence behavior and the structure properties by using FTIR and Raman spectroscopy in these glass systems as a function of co-dopant concentration.

## ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support from Ministry of Higher Education in Kurdistan Region Government (KRG) in Iraq, and the financial support from Ministry of Higher Education, RMC, UTM and etc., through the research grant (vote 4B185) are highly appreciated.

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