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Optical Absorption of Er^{3+}/Nd^{3+} Co-Doped Tellurite Glass

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Abstract. Tellurite glasses of varying Er^{3+}/Nd^{3+} concentration were successfully prepared by melt-quenching method. The X-Ray diffraction pattern was determined by using Siemens Diffractometer D5000 while the optical properties were measured using Shimadzu 3101 pc UV-VIS NIR scanning spectrophotometer. It was found that the diffraction patterns of all samples showed glasses characteristics. The optical band gap, E_{opt} increased proportionally with the content of Er_2O_3 but Urbach energy, ΔE decreased due to the increasing Er_2O_3 contents.

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, 2]. 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 raising of the temperature [3].

Sudhakar et al. [4] recently reported that one chalcogen (Te) element could significantly enhanced the transmission capability, moisture resistance and transparency in the UV and IR wavelength regions for their use as optical materials with suitable dopant 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 fiber amplifier, visible laser, optical data storage, sensors and optical communication devices [5, 6].

However, the high concentration of dopant quenches the performance of amplifiers and laser [7, 8]. Improving the up-conversion emission and the quantum efficiency is the key issue. Not many studies on the characteristics of tellurite glass co-doped with Er_2O_3 and Nd_2O_3 exists in the literature. The mechanism behind the up-conversion emission and concentration quenching is still debatable. In view of the above, we have attempted to examine the role of co-doping on thermal and optical properties of tellurite glasses. In this work, the optical properties of Er^{3+}/Nd^{3+} co-doped tellurite glass system were examined systematically employing spectroscopic techniques.

Experimental Details

The glass samples were prepared by rapid melt quenching method. The series of five binary glass system (designated as S1 to S5) consist of $(78\text{-}x)TeO_2$ - $10Li_2O$ - $10MgO$ - $2Nd_2O_3$ - $(x)Er_2O_3$ with x = 0.4 to 2.0 mol % are presented in Table 1. About 20 g batches of homogenized starting materials of each component were placed in a platinum crucible before being melted in a furnace at 900 ^oC for 30 min. After the required viscosity was achieved the melt were then casted on a metal plate before being annealed at 260 ^oC for 3 h. Finally, the temperature of the furnace was reduced to room temperature allowing the sample to cool down.

Powder X-Ray diffraction was determined using CuK_α radiation operating in Bragg–Brentano geometry at room temperature using the Siemens Diffractometer D5000 that confirmed the amorphous nature of the glass samples. The UV-Visible absorption spectra of the samples were recorded at room temperature by using a Shimadzu 3101 pc UV-VIS NIR scanning spectrophotometer in the wavelength range of 200 - 2800 nm. The bulk glass samples of two parallel polished faces having uniform thickness of 2 mm were used for the measurements.

Results and Discussion

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+} codoped tellurite glass.

Glass sample	Mol fraction (mol %)		Optical band gap	Urbach energy, ΔE
	Er_2O_3	TeO_2	E_{opt} (eV)	(eV)
S1	0.4	77.6	2.003	0.046
S2	0.8	77.2	2.008	0.043
S3	1.2	76.8	2.020	0.034
S4	1.6	76.4	2.025	0.031
S5	2.0	76.0	2.028	0.029

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 $(78\text{-}x)TeO_2\text{-}10Li_2O\text{-}10MgO\text{-}2Nd_2O_3\text{-}xEr_2O_3$ glass system structures were tested by means of X-Ray diffraction. The diffraction patterns (Fig. 1) of all samples showed broad humps over the region 20-35º for 2Θ values, which confirm the amorphous nature in the glasses characteristics [9].

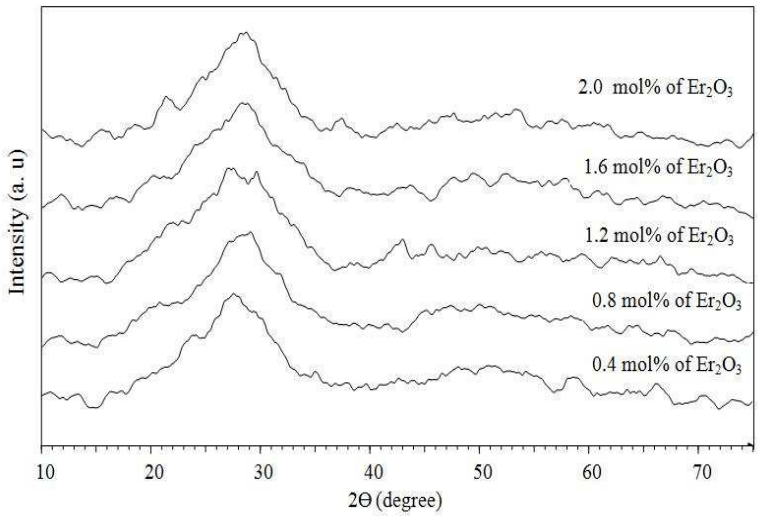


Fig 1. XRD patterns of $(78\text{-}x)TeO_2\text{-}10Li_2O\text{-}10MgO\text{-}2Nd_2O_3\text{-}(x)Er_2O_3$ glasses.

The study of absorption edge in the UV region provides useful information towards the investigation of optical induced transitions, optical band gaps and electronic band structures in crystalline and non-crystalline 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 involve 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. The absorption coefficient (ω) in amorphous materials is given by Davis and Mott as a function of photon energy (ħω) for the direct and the indirect transition [10].

The relation between (ω) and photon energy of the incident radiation can be written as [11, 12]:

$$\alpha(\omega) = \frac{A(\hbar\omega - E_{opt})}{\hbar\omega} \quad (1)$$

where A is a constant and $\alpha(\omega)$ is the absorption coefficient at an angular frequency $\omega = 2\pi\nu$, ħ is the Planck constant divided by 2π and n is an index which can take values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. The values of n is equal to 1/2 for allowed direct transitions, 3/2 for direct forbidden transitions, 2 for allowed indirect transitions and 3 for forbidden indirect transitions. Using Eq. (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 samples as represented in Fig. 3(a).

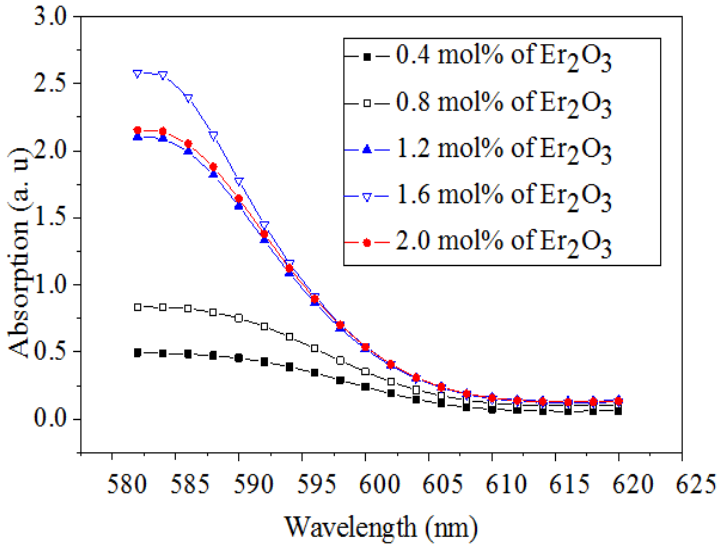
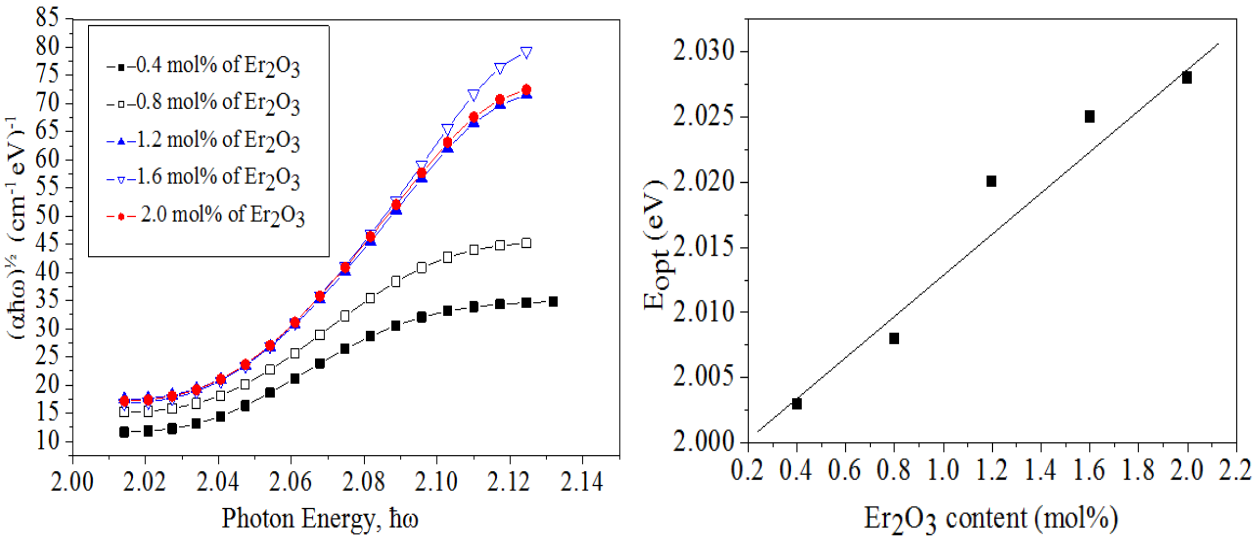


Fig 2. Variation of absorption coefficient with wavelength for different Er_2O_3 mol %



(a) (b)

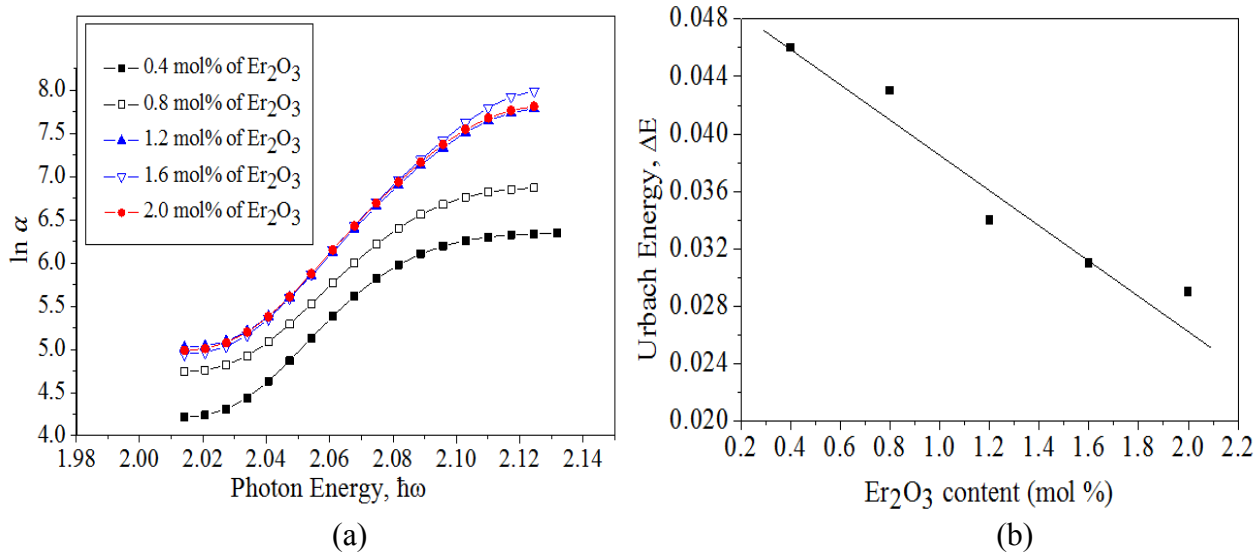
Fig 3. (a) A plot of $(\alpha\hbar\omega)^{1/2}$ versus photon energy (ħω) for all the samples and (b) A plot of Optical band gap against Er_2O_3 content (mol %)

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 increase of the optical band gap as the Er_2O_3 content is increased (decreasing TeO_2). These values were less than the ternary tellurite glass [13]. This result shows that the covalent nature of the glass matrix decrease with increase of TeO_2 concentration [14, 15].

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 [12, 16],

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

where C is a constant and ΔE is the Urbach energy.



(a) (b)

Figure 4: (a) A plot of ln α against photon energy, ħω and (b) plot of Urbach Energy, ΔE against Er_2O_3 content (mol %).

The value of Urbach energy was between 0.046 and 0.029 eV (Table 1). A plot ΔE against Er_2O_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 decreases as the Er_2O_3 concentration increases. The much lower value of Urbach energies observed for the present glasses suggest that the defects in these glasses are minimum [15]. Our 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 [15]. The lowest values Urbach Energy (ΔE=0.029 eV) was observed for the S5 glass.

Conclusion

The role of co-doping on optical of tellurite glasses with composition (78-x)TeO_2-10Li_2O-10MgO-2Nd_2O_3-(x)Er_2O_3 (x = 0.4 to 2.0 mol%) were investigated. The amorphous nature of the prepared samples by melt-quenching method is confirmed by XRD. The Optical absorption behaviour 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 decreased with increasing of Er_2O_3 contents. The decrement 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. Our results are in conformity with other findings. The mechanism of the glass forming ability is understood. It is interesting to look at the fluorescence quenching in these glass systems as a function of co-dopant concentration and temperature.

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