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Studies of Physical and Optical Behavior of Er^{3+}/Yb^{3+} Co-doped Titanium Tellurite Glasses

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Abstract: The Er_2O_3-Yb_2O_3 codoped TeO_2-TiO_2-Na_2O-glasses have batch compositions of (70-x-y) %TeO_2-20%. TiO_2-10% Na_2O-x% Er_2O_3-y% Yb_2O_3 have been prepared successfully by using the conventional melt quench technique, where (x, y) are (0, 1, 1) and (0, 1, 2). Differential scanning calorimetry (DSC) is used to measure the glass transition temperature of synthesized samples. X-ray Diffraction studies were made on these glass samples at room temperature. The amorphous nature of the prepared glass samples was confirmed from the XRD patterns. The density of prepared glass samples was determined by using the fluid displacement method, which is based on the Archimedes principle. Other physical properties of synthesized glass sample such as molar volume (V_m), titanium ion concentration (N), Polaron radius (R_p), inter nuclear distance (R_i), molar refractivity (R_m), Oxygen Packing density (OPD) and field strength (χ) were calculated. The UV-Visible absorption characterizations of synthesized glasses with varying Er_2O_3/Yb_2O_3 doping percentages were carried out in the 400–1000 nm range. Glasses optical characteristics, including their absorption coefficient (α), refractive index, the band gap energies for both direct and indirect possible transitions and the Urbach energies (Eu) have been studied from the absorption spectra. The impact of Er_2O_3/Yb_2O_3 and effect of thickness on optical characteristic is observed.

Keywords: Rare Earth Doped Glass, X- Ray Diffraction, Optical Properties, Absorption Spectra, Urbach Energy

1. Introduction

For photonic applications such as optical fibres, solid-state lasers, waveguides, optical amplifiers, optical modulators, optical temperature sensors, and frequency doubling [1–5], rare earth-doped tellurite-based glass systems are attractive materials. This particular form of matrix exhibits beneficial optical qualities over other glasses, including high linear and nonlinear refractive indices, a low phonon energy (700 cm^{-1}), a broad range of optical window transparency, and better rare earth solubility than oxide glasses [6]. Additionally, this glass has a low melting point temperature, strong thermal resilience, and chemical inertness [7].

The industry is expanding as a result of technological advancements and policies favoring renewable energy sources [8]. Two methods are typically investigated to boost efficiency: the first is based on the hunt for novel materials or methods that can explore the photovoltaic effect effectively, and the second is associated with solar spectrum alteration to align it with the spectral efficiency of solar cells. In the first instance, innovative materials including thin-film technologies and organic solar cells were examined and their potential was discussed [9, 10]. Numerous studies have been published on the lighting and optical thermometry characteristics of various Er^{3+} doped or Er^{3+}/Yb^{3+}codoped glass materials. [11–14]. It is widely established that the characteristics of Er^{3+} emission depend on the contents of both Yb^{3+} and Er^{3+} and are significantly impacted by the optoelectronic properties of the host material. Tellurite glasses have greater advantages than silicate and borate glasses because of their physical characteristics, which include a low melting point, a high dielectric constant, a significant third-order nonlinear sensitivity, and good infrared transmissivity. Additionally, they exhibit significant transparency from the near ultraviolet to the middle infrared spectrum. They may incorporate significant amounts of rare-earth ions into the matrix and are resistant to ambient humidity [15–18]. The linear and nonlinear refractive indices are also increased by the addition of TiO_2. Large radiative transition probabilities result from a high linear index's enhancement of the local field correction at the rare-earth site, whereas a high nonlinear index boosts optical nonlinearities [19–21]. Because of its uses as well as the fact that its spectroscopic properties vary with composition compared to other trivalent rare-earth ions, Erbium /Ytterbium ions are the most extensively researched rare-earth ion in a range of glasses [22]. The concentration and ratio of Erbium /Ytterbium ions dopants must be optimised because these factors will determine the device's overall effectiveness while exploring Erbium /Ytterbium ions co-doped material. The purpose of this research is to (i) acquire tellurite glasses co-doped with Er^{3+}/Yb^{3+}glass transition temperature Tg for the creation of a temperature optical sensor and (ii) examine the optical, structural, and thermal characteristics of the glasses as a consequence of the TiO_2 content. TeO_2-TiO_2-Na_2O, Yb_2O_3, and Er_2O_3 were carefully chosen components for the matrix that was provided to order to enhance this feature. The best of these glasses will then be chosen for a subsequent investigation aimed at their potential use as photonic materials. Future studies will focus on determining these glasses' optical characteristics.

2. Materials and Method

The samples of titanium tellurite glass co-doped with Er^{3+}/Yb^{3+} have a composition of (70-x-y) %. TeO_2-20% TiO_2-10% Na_2O-x% Er_2O_3-y%Yb_2O_3 was prepared using the traditional melt-quenching method, where (x, y) are (0, 1, 1) and (0, 1, 2) in mol%. Tellurium oxide (TeO_2), titanium oxide (TiO_2), and sodium oxide (Na_2O) were used as starting batch components to make RE's Er^{3+}/Yb^{3+} co-doped oxide glass samples. The oxide powders' purities are 99.995% for TeO_2 (Otto), 99.999% for TiO_2 (Otto), 99.99% for Yb_2O_3 (Otto), 99.99% for Er_2O_3 (Otto), and 99.999% for Na_2O (Otto). Using a mortar and pestle prepared batches are crushed to produce a homogenous mixture. The batches are placed in an alumina crucible and heated to 900^0 C in a muffle furnace. The glassy melt is removed from the muffle furnace, mechanically stirred, and then placed again into the muffle furnace for 30 minutes to reach a temperature of 960^0 C. Pallets are formed by pouring the glassy melt into the mould. To remove stress, Synthesized samples are heated to 350^0 C in an oven. Different types of characterizations have been carried out for the physical and optical studies. Differential scanning calorimetry (DSC) was used to perform thermal analyses of synthesized samples. Using a Bruker Model No. D2 Phaser 2nd Gen, an X-ray Diffractogram is used to determine the molecular arrangement of samples. Absorption spectroscopy is used to investigate the optical characteristics of prepared samples doped with rare earth ions. Absorption spectrum is recorded between the range of 400 nm to 1000 nm by using spectrometer model no. RI2SA (Research India).

3. Results and Discussion

3.1. X-ray Diffraction

The Er3+/Yb3+ co-doped titanium tellurite glasses X-ray diffraction pattern was reported in the $10° \leq \theta \leq 80°$ range. XRD patterns for the TTN, TTNEY1 and TTNEY2 glasses are presented in Figure 1. From the figure, it can be seen that the X-ray diffraction pattern of the prepared glass samples are similar and absent sharp diffraction peak but can see the broad humps near the angle 30° which is the characteristic of amorphous materials [23].

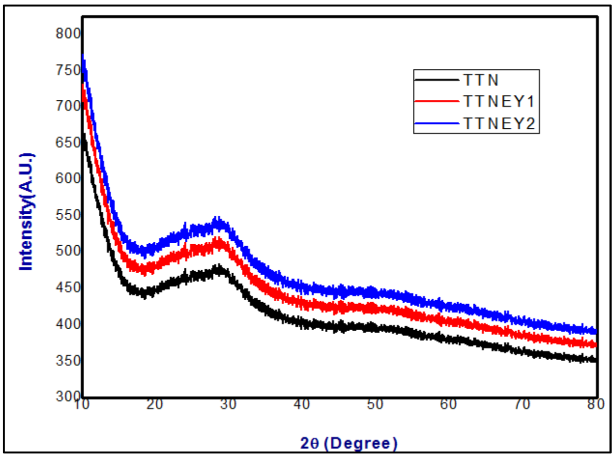

Figure 1. *XRD pattern of TTNEY glasses.*

3.2. DSC

Figure 2 shows DSC plot of the titanium tellurite glass samples doped with Er^{3+}/Yb^{3+} (TTNEY) with batch composition (70-x-y) % TeO_2-20% TiO_2-10% Na_2O-x% Er_2O_3-y%Yb_2O_3. Using TA instruments USA, Q10, in the temperature range of 40 °C to 440 °C at a heating rate of 10 °C/min, the thermal characteristics of the prepared samples TTN, TTNEY1 and TTNEY2 were investigated. The titanium tellurite glasses TTN, TTNEY1 and TTNEY2 have glass transition temperatures of 360°C, 335°C and 340°C respectively.

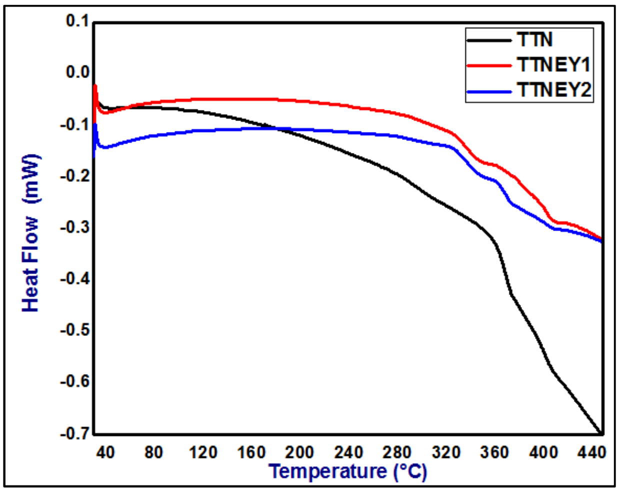

Figure 2. *DSC curves of TTNEY glass sample.*

3.3. Physical Parameter Measurements

The synthesized glass sample's physical characteristics including density (ρ), molecular mass (M), molecular volume (Vm), (OPD), titanium ion concentration (N), polaron radius (Rp), and inter nuclear distance (Ri), were calculated are shown in Table 1. Calculating glass density is the simplest physical property. It was calculated using purified water as the immersion liquid at room temperature and the fluid displacement method, which is based on the Archimedes principle. The weight of the displaced fluid equals the buoyancy, in accordance with the Archimedes principle. The following relation was used to determine the density:

$$\rho = \left(\frac{\mathrm{wair}}{\mathrm{wair}-\mathrm{wliq}}\right) \quad (1)$$

Distilled water's density is ρ_{liq} and the masses of TTN, TTNEY1, and TTNEY2 glass in air and distilled water are w_{air} and w_{liq}.

The molecular weight and calculated densities were used to determine the molar volume (Vm) of TTNEY glasses.

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

The glass sample's molar volume (Vm) and the number of oxygen atoms (n) that are present influence the oxygen packing density (OPD). The following relation was used to determine the OPD [24].

$$\mathrm{OPD} = \frac{1000\times n}{Vm} \quad (3)$$

Using the relation, the concentration of titanium ions in glass samples 'N (ion/cm3) was calculated. [25, 26]

$$\mathrm{N} = \frac{\text{mole\% of }\mathbf{Ti}\text{ ions }\times\rho\times \mathrm{NA}}{\mathrm{Vm}} \quad (4)$$

Where 'NA' is Avogadro number. The polaron radius (Rp) and inter nuclear distance (Ri) are calculated by using ion concentration [27].

$$\mathrm{Rp} = \tfrac{1}{2}\,(6\pi \mathrm{N})^{1/3} \quad (5)$$

$$\mathrm{Ri} = (1/\mathrm{N})^{1/3} \quad (6)$$

The density values increased from 4.997 to 5.031 g/cm3 with the increasing of Er^{3+}/Yb^{3+}concentration. From the results of molar volume and density, the average Ti-Ti distance, titanium ion concentration (N), Polaron radius (R_p), inter nuclear distance (R_i), Oxygen Packing density (OPD) and field strength (χ) were calculated and are given in Table 1. It is also observed (Table 1) that the field strength (χ) and inter ionic distance (R_i) decreased with increasing of Er^{3+}/Yb^{3+}concentration. While the polaron radius (R_p) and molar refractivity (R_m) increases with increasing of Er^{3+}/Yb^{3+}concentration. Molar volume fell from 26.8561 to 27.5821 cm3/mol. Molar volume explains the glass structure better than density since the latter concerns the spatial distribution of ions in the structure.

Table 1. *Measured physical parameters of (70-x-y) %TeO_2-20%TiO_2-10%Na_2O-x%Er_2O_3-y%Yb_2O_3glasses.*

Name Of the Sample	TTN	TTNEY1	TTNEY2
Chemical Composition of (70-x-y)%TeO_2-20%TiO_2-10%Na_2O-x%Er_2O_3-y%Yb_2O_3	70:20:10:0:0	68:20:10:1:1	67:20:10:1:2
Molar Mass (M) gm/mol	134.2	137.65	138.76
Density ρ (g/cm^3)	4.997	5.015	5.031
V_m (cm^3/ mol)	26.8561	27.4482	27.5821
OPD (mol/l)	103.1698	101.3485	102.3744
RE concentration ($\times10^{20}$) (ions cm^{-3})	-	6.7242	8.8782
R_p (nm)	-	0.1889	0.27069
R_i (nm)	-	1.141×10^{10}	1.041×10^{10}
Rm (cm^3)	16.4582	16.8211	16.9032
(χ) Field Strength	-	2.3026×10^{14}	2.2713×10^{14}

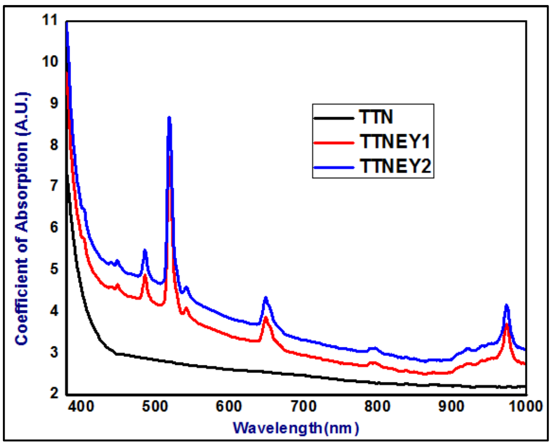

Figure 3. *Absorbance plot for TTNEY glass samples.*

3.4. Optical Properties

Optical properties UV-Visible-IR absorption spectra of synthesized glasses of composition (70-x-y) %TeO_2-20%TiO_2-10%Na_2O-x%Er_2O_3-y%Yb_2O_3were carried in the wavelength range from 400nm to1000nm taken at ambient temperature (shown in Figure 3). The following relation gives the absorption coefficient α of glass of thickness t. [28]

$$\alpha = 2.302A/t \quad (7)$$

where A is the sample's absorbance.

In amorphous materials, it is well known that the absorption coefficient α depends on hv according to the following equation (8) [29].

$$\alpha\ hv = \mathrm{A}\,(hv - E\,\mathrm{g})^{\mathrm{r}} \quad (8)$$

where, “A” represents the proportionality constant and Eg is the optical band gap, and m is the power indicated in the transition process. If r = 2, it is direct allowed transition. If r = 1/2, it is indirect allowed transition. respectively. Therefore, to calculate the direct optical band gap in all titanium tellurite glasses doped with Er^{3+}/Yb^{3+}, r = 1/2 has been considered in equation 8. The curves between $(\alpha h\nu)^2$ versus incident radiation energy “hν (in eV)” for all the TTN glasses are shown in Figure 4. In order to investigate the optical band gap values, the linear portion of the illustrated curves up to (αhν)2 = 0 was extrapolated. For all the prepared TTN, TTNEY1 and TTNEY2 glasses are found to be 3.0, 2.94 and 2.9 eV in table 2.

Table 2. *Optical properties of (70-x-y) %TeO_2-20%TiO_2-10%Na_2O-x%Er_2O_3-y%Yb_2O_3 glasses.*

Name Of The Sample	TTN	TTNEY1	TTNEY2
Chemical Composition of (70-x-y)%TeO_2-20%TiO_2-10%Na_2O-x%Er_2O_3-y%Yb_2O_3	70:20:10:0:0	68:20:10:1:1	67:20:10:1:2
Direct energy bandgap (eV)	3.0	2.94	2.9
Indirect energy band gap (eV)	3.0	2.95	2.92
Refractive index	2.040	2.051	2.055
Urbach energy (eV)	0.26	0.28	0.30

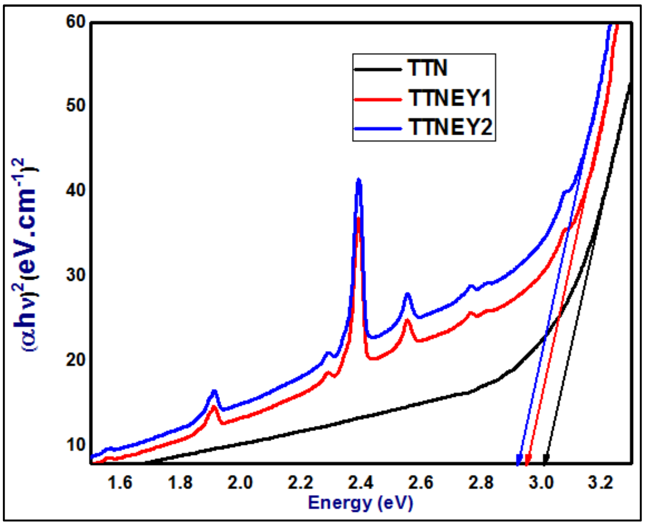

Figure 4. *Tauc's plot for direct forbidden energy gap for TTNEY glass samples.*

Now the curves between $(\alpha h\nu)^{1/2}$ versus incident radiation energy “hν (in eV)” for all the TTN, TTNEY1 and TTNEY2 glasses are shown indirect band gap in Figure 5. the optical band gap values are found to be 3.0, 2.95, and 2.92 eV in table 2.

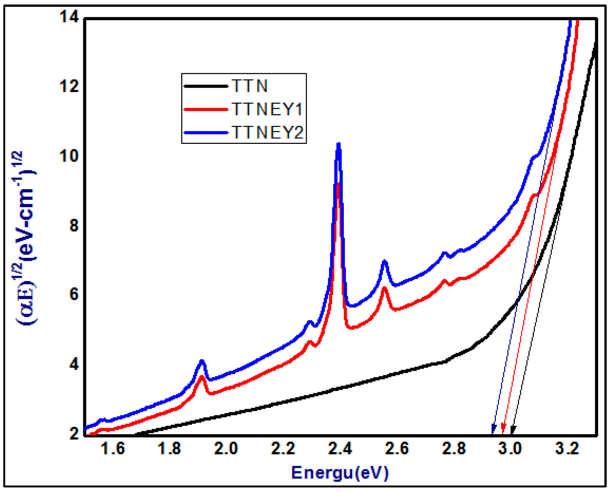

Figure 5. *Tauc's plot for indirect forbidden energy gap for TTNEY glass samples.*

The following relation can be used to calculate the refractive index "n" [30].

$$(n^2 - 1)/(n^2 + 1) = 1 - \sqrt{(Eg/20)} \quad (9)$$

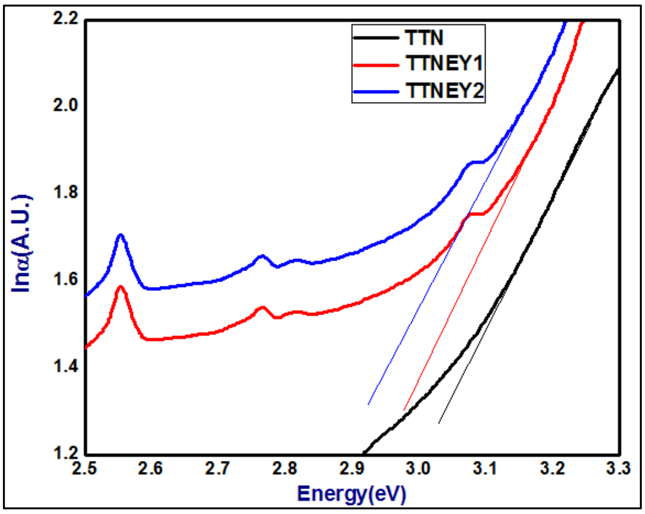

Figure 6. *Urbach's plot for TTNEY glasses.*

The relation between the incident photon energy and the absorption coefficient can be expressed as [31].

$$\alpha = \alpha_0 e^{h\nu/Eu} \quad (10)$$

where, α_0 is proportionality constant Eq. (10) can be rewrite as

$$\ln \alpha = h\nu/Eu + constant \quad (11)$$

For all of the prepared glass samples, curves are drawn between logarithmic values of the absorption coefficient vs incident photon energy, demonstrating the exponential behavior given in equation 10. The Urbach's plot, which shows the relationship between energy hν and lnα can be used to calculate the value of Eu as the reciprocal of the slope in the cutoff region. The disorderness of the structure-controlled Eu. Figure 6 shows the Urbach's plot for the TTN, TTNEY1, and TTNEY2 glasses. Table 2 shows the evaluated values.

4. Conclusion

Titanium tellurite glass co-doped with Er^{3+}/Yb^{3+} have a composition of (70-x-y) %. TeO_2-20% TiO_2-10% Na_2O-x% Er_2O_3-y%$Yb_2O_3$where (x, y) are (0, 1, 1) and (0, 1, 2) were prepared successfully using conventional melt quenching method. The low transition temperature of synthesized titanium tellurite glasses was confirmed by DSC characterization. XRD confirmed the amorphous nature of the prepared glass samples. From the results density and R. I. of samples are quite high 5.031 gm/cc, and 2.055. It is also observed (Table 1) that the field strength (χ) and inter ionic distance (R_i) decreased with increasing of Er^{3+}/Yb^{3+}concentration. While the polaron radius (R_p) and molar refractivity (R_m) increases with increasing of Er^{3+}/Yb^{3+}concentration. Molar volume fell from 26.8561 to 27.5821 cm3/mol. Molar volume explains the glass structure better than density since the latter concerns the spatial distribution of ions in the structure. Through UV-VIS-NIR spectroscopy, the samples' optical absorption behaviour is measured. It was observed that the maximum value of both of the optical band gap (E I opt. =3.0eV) for TTN sample and Urbach energy (ΔE=0.3eV) for the third sample TTNEY2. Both the optical band gap and the Urbach energy are found to be strong analytical functions of the co-dopant concentration. And also justify its candidature for photonic devices. The information provided in this work may open up the possibility of future development of glasses made of titanium tellurite that has been doped with Er^{3+}/Yb^{3+}.

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