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OPTICAL ABSORPTION SPECTRA OF SAMARIUM DOPED TeO_2-Na_2O GLASSES

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ABSTRACT

In this paper the modification of optical absorption spectra characteristics of tellurite glasses doped by Sm^{3+} ions has been studied. Sodium-tellurite glasses have a composition (80-x) TeO_2-20Na_2O-$x$$Sm_2O_3$ with concentration (x=0, 0.3, 0.6, 1, 1.2, 1.5) were synthesized by melt-quenching technique. Physical and optical parameters are calculated from absorption spectra and by measuring the density of the samples. The maximum density is found to be (5.019 g cm^{-3}) for 1.2 mol% of Sm^{3+} ions. The variations in the polarizability (4.758-4.863 cm^3) and the molar volume (28.359–28.919 cm^3mol^{-1}) with dopant concentration are ascribed to the formation of non-bridging oxygen. This observation is consistent with the alteration of number of bonds per unit volume. The amorphous nature of the prepared glasses were confirmed by using x-ray diffraction (XRD) pattern. The UV spectra of the prepared sample have been measured at room temperature and at a wavelength range 200-1000 nm. The recorded absorption spectra exhibit nine absorption picks represented by transition bands $^6H_{5/2}\rightarrow{}^6P_{3/2}$, $^4I_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6H_{15/2}$ and $^6F_{1/2}$. The values of the optical band gap are found to lie between 3.044 eV -3.186 eV, while Urbach energy (E_u) values varies between 0.312 eV -0.209 eV. The optical energy gap for indirect forbidden transition has increased whereas the values of Urbach energy have decreased with the increasing of Sm_2O_3 content. The absorption cut-off wavelength (λ_c) in the range 360.8nm-366.15nm calculated from the UV spectra and it depend on the Sm^{3+} concentration, the optical properties were found to be strongly affected by the varying concentration of Sm^{3+} ions.

Keywords: Telluride glass; Sm_3O ion; Absorption Spectra; Optical Energy Band Gap;

INTRODUCTION

The optical behavior of the RE-doped glasses is one of the most important studies in this area. Therefore, several spectroscopic analyses are recommended to achieve the complete optical properties of any glass system. The main purpose of studying the

optical absorption are to explain the spectra characteristics such as spectra shape, shifts of the absorption edge, absorption pick intensity and transition bands. This method is very useful for giving the illustration about the mechanism of optically-induced transitions and the knowledge about the band modification in crystalline and non-crystalline materials. Absorption of glasses have become important field for studying the interaction of glass material with radiation and the absorption of a photon with a large energy has been studied for many decades [1]. Recently, different rare earth ions were doped into tellurite glasses, the optical properties of these glasses have been investigated widely and most of the results have contributed to commercial applications.

Trivalent lanthanide ions doped with a heavy metal oxide based on tellurite glasses have been prepared for a different range of concentration and compositions, these glasses found to be suitable for a wide area of applications in the fields of lasers and telecommunications. Low phonon energy is another property of the tellurite glasses, this mean that tellurite as a host glasses with low phonon energies will allow high number of radiative transition rates that are useful for the design and development of several types of optical devices such as up converters, light emitting diodes (LEDs), fiber amplifiers, memory devices, etc. In this direction, a great amount of research has been carried out to develop new glass matrices containing rare earth (RE) ions [2]. Different individual properties of tellurite glasses considered as a favorable materials for linear and non-linear optical applications, because they exhibits a good attention due to their low phonon energy, high refractive index and low melting temperature [3]. Because of the low transition temperature and excellent infrared transmission, therefore, tellurite glasses are potentially candidate for various longer wavelength applications [4,5]. In spite of, many studies on the absorption characteristics of Sm^{3+} ions in the UV-VIS-NIR regions but argumentative still questionable. Our objective in the present work are to investigate the absorption spectra of the prepared glass samples and to examine the role of Sm^{3+} ions on the optical band gap and Urbach energy of these glasses.

EXPERIMENTAL

Glass samples with a high purity 99.9% from Sigma Aldrich company were prepared with a chemical composition $(80\text{-}x)TeO_2\text{-}20Na_2O\text{-}xSm_2O_3$ at (x=0,0.3,0.6,1.1.2,1.5), all raw materials weighed with an accurate 4 digit electronic balance then the composition mixed together by using a milling machine, the glass sample code and their molar ratio of the material composition are presented in Table 1. Glass samples are synthesized by a conventional melt-quenching technique, samples were prepared for graining and polishing until the appropriate thickness (2.5mm±0.01) achieved. Very fine powders of samples are used to measure the x-ray diffraction pattern of tellurite glasses. The Bruker D8 Advance diffractometer using *CuKα* radiations (λ=1.54 A^o) at 40kV and 100 mA was used to perform the experiment. The optical absorption of the prepared samples measured at a room temperature by using UV-VIS-NIR (Model: UV-1301PC) spectrophotometer and the used wavelength range was 200-1000 nm.

Table 1: Glasses sample code and their concentration ratio

Sample Code	TeO_2 %	Na_2O %	Sm_2O_3 %	Molar Mass [g mol^{-1}]
TNS1	80	20	0	140.07
TNS2	79.7	20	0.3	140.64
TNS3	79.4	20	0.6	141.21
TNS4	79	20	1	141.97
TNS5	78.8	20	1.2	142.34
TNS6	78.5	20	1.5	142.91

RESULTS AND DISCUSSION

Physical Parameter

Density of the glass sample was determined by using Archimedes' method, the weight of the sample was measured by using an accurate 4 digit sensitive analytical electronic balance Precisa XT220A, toluene was used as an immersed liquid with the density (ρ_t=0.8669 g cm^{-3}) at room temperature. The density ρ is calculated using the expression [6]:

$$\rho = [(\frac{W_a}{W_a - W_t}) * \rho_t + \rho_a] \quad (1)$$

Where W_a and W_t are weight of the glass sample in air and in toluene respectively, ρ_a is the density of air and ρ_t is the density of the toluene. The molar volume (V_M) of the glasses was calculated depending on the density values according to [7]:

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

where M is the molar weight and ρ is the density of the glass. By using Makishima and Mackenzie approach we can calculate the ionic packing density (V_t) [7,8],

$$V_t = \left(\frac{1}{V_M}\right) * \sum(V_i * x_i) \quad (3)$$

where x_i is the mole fraction (mol%) and V_i is packing density parameter (m^3/mol). For an oxide glass of the form M_xO_Y, the value of V_i yields [8],

$$V_i = \left(\frac{4\pi N_A}{3}\right)[Xr_M^3 + Yr_o^3] \quad (4)$$

where N_A is Avogadro's number (mol^{-1}), r_M and r_o are the Shannon's ionic radius of metal and oxygen, respectively. The refractive index (n) of glass in terms of optical band gap (E_{opt}) is obtained by using [9,10]

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_{opt}}{20}} \quad (5)$$

The molar refractivity (R_M) can be obtained from [11],

$$R_M = \frac{n^2-1}{n^2+2}(V_M) \quad (6)$$

Polarizability (a_e) is related to the refractive index through the Lorentz-Lorentz equation and can be expressed as [11],

$$\frac{n^2-1}{n^2+2}(V_M) = \frac{4}{3}\pi N_A \alpha_e \quad (7)$$

Where N_A is the Avogadro's number. The effects of Sm^{3+} ion on the physical properties

of glass samples are summarized in Table 2. The effect of Sm_2O_3% on both of the density and molar volume for each composition of the glass samples is shown in Figure 1, from Figure 1 it can be seen that the density of TNS glass system increases from 4.903 g cm^{-3} for x=0 mol% to 5.019 g cm^{-3} for x=1.2 mol% of Sm^{3+} ion. Higher molecular mass of Sm_3O_2 (348.74 g mol^{-1}) and those for TeO_2 (159.60 g mol^{-1}) might be responsible for increase its density [12]. The decrease in density at x=1.5 mol% might be caused by Sm^{3+} ions which take a part in the structure of glass and make the density to be decreased [13]. A molar volume of the TNS glass system which is plotted against Sm_2O_3 % in the Figure 1 reveals that the molar volume increased from TNS1 to TNS3 glasses as the Sm^{3+} content increased from 0 mol% to 0.6 mol%, while the molar volume of glass TNS4 and TNS5 decreased with increasing of Sm^{3+} content, this effect can be explained as the Sm^{3+} mole friction content more increased the structure of glasses will get more compact due to increase in packing density of oxygen [14] and this indicates that the structure of TNS glasses changed, this behavior of molar volume is in consistent with the increasing behavior of rigidity and compactness of glass samples [15]. Table 2 represents measured and calculated physical parameter for prepared glass with different composition,

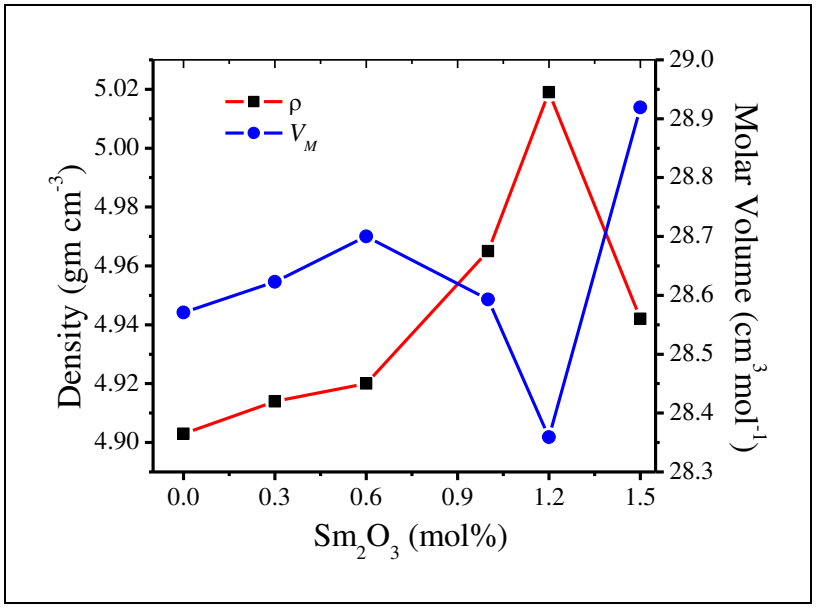


Figure 1: Density and molar volume as a function of Sm^{3+} ions mol%.

Table 2: effect of Sm^{3+} ion on physical properties of glass samples

Sample Name	ρ [gm cm^{-3}]	V_M [cm^3 mol^{-1}]	V_t	n	R_M [cm^3mol^{-1}]	$\alpha_e \times 10^{-18}$ [cm^3]
TNS1	4.903	28.571	0.4012	2.385	17.424	4.839
TNS2	4.914	28.623	0.4017	2.354	17.233	4.786
TNS3	4.920	28.700	0.4019	2.349	17.245	4.790
TNS4	4.965	28.593	0.4051	2.355	17.224	4.784
TNS5	5.019	28.359	0.4092	2.362	17.131	4.758
TNS6	4.942	28.919	0.4025	2.367	17.509	4.863

Figure 2 shows the change in refractive index value by increasing Sm^{3+} ion, this effect ascribed to the notable modifications in the glass network structure and the change in refractive index also depicts higher polarizability [16,17]. The change in molar refraction by increasing Sm^{3+} ion is shown in Figure 3, this relation is due to the proportionality with the material polarizability [18].

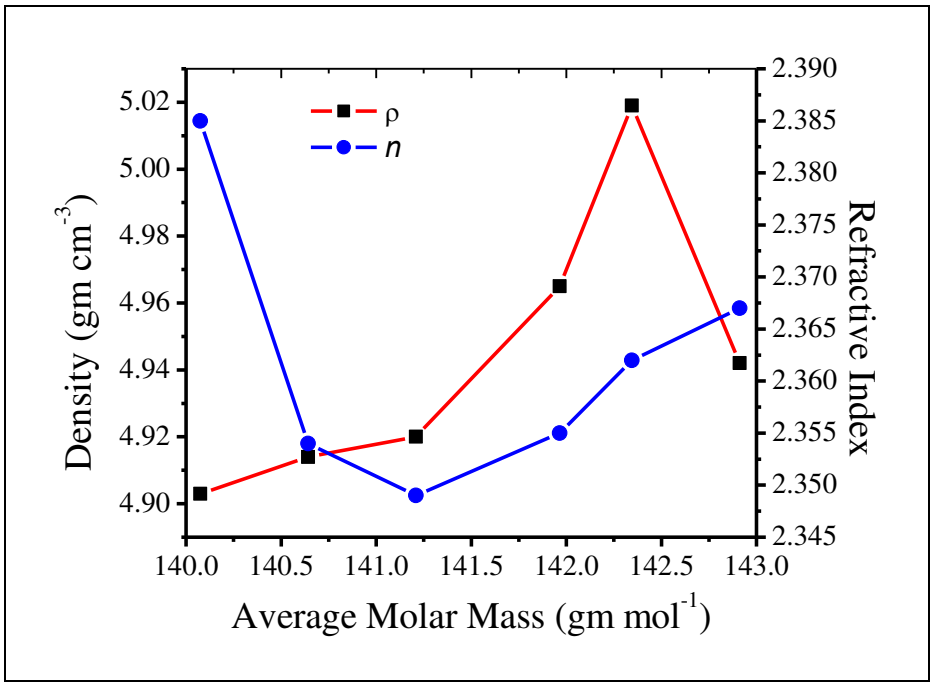


Figure 2: Density and refractive index as a function of average molar mass of the glass sample

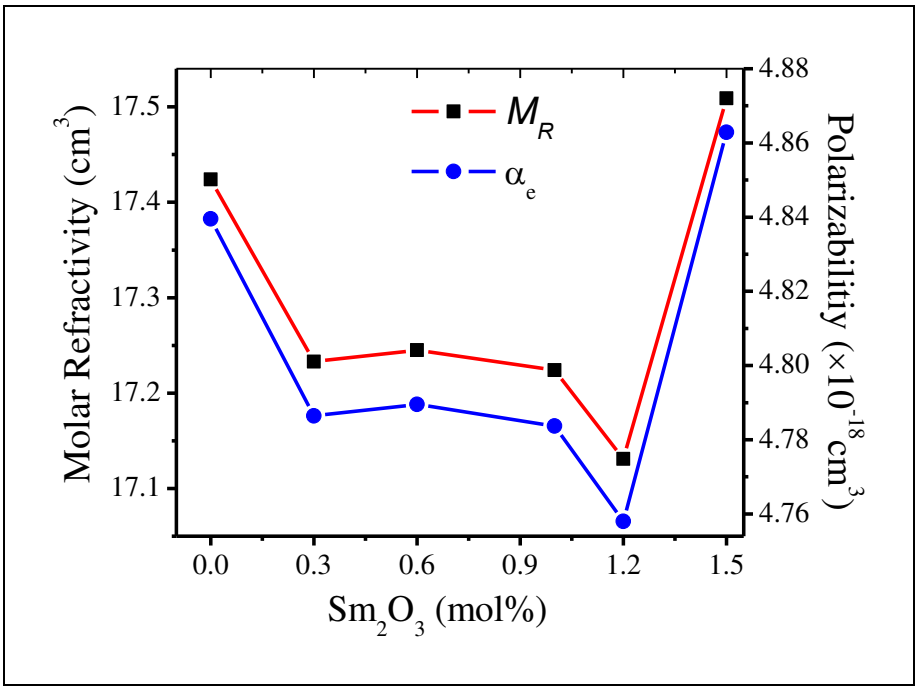


Figure 3: Molar refractivity and polarizability as a function of Sm^{3+} ions mol%

XRD Pattern

The amorphous phase nature of the glass samples were illustrated by using the XRD technique. Figure 4 shows the XRD pattern of the prepared glass sample, we observed a broad halo at around 20-40 degree for all samples, the absence of any sharp peak indicates that samples are exhibits amorphous nature [19].

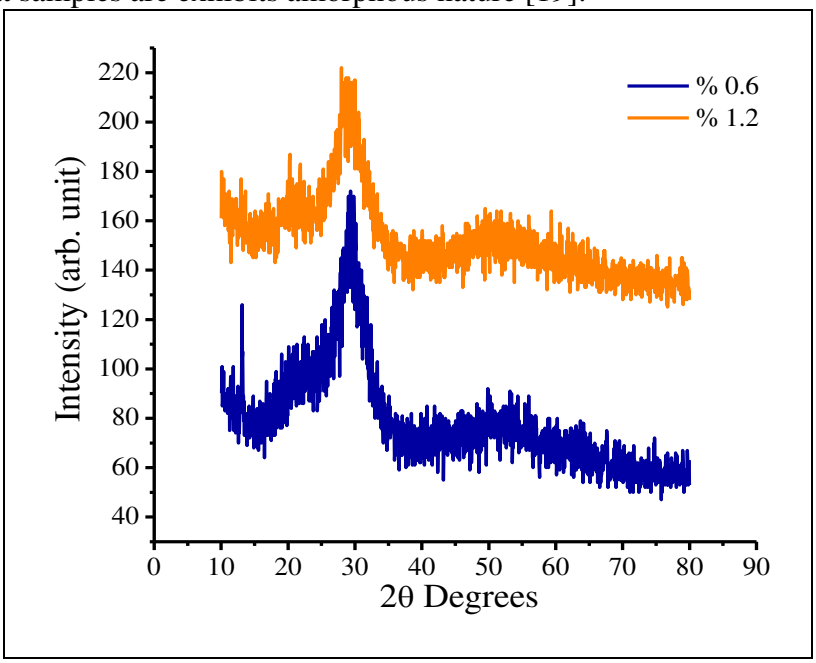


Figure 4: Typical XRD pattern of TNS2 and TNS4 glasses sample system

Band Gap and Urbach Energy

The absorption spectra of (80-x)TeO2-20Na_2O-xSm_2O_3 at (x=0,0.3,0.6,1.1.2,1.5) glasses recorded at room temperature are shown in Figure 5. the absorbance dramatically drop in the UV regions of 200-400 nm which showing the high energy absorption around 300 nm [20]. Typically nine absorption bands with different relative intensities have been observed around 401, 474, 948, 1086, 1239, 1386, 1490, 1552 and 1597nm respectively corresponding to transition bands $^6H_{5/2}$ ground state to $_6P3_{/2}$, $^4I_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6H_{15/2}$ and $^6F_{1/2}$ excited state, the intensities of the corresponding bands are found to vary from glass to glass. The derived energy levels were found to be in agreement with those reported for other Sm^{3+} doped glasses [21,22,23]. The absorption pick wavelength normalized by the sample thickness of the glass and the assignments of the bands for the excited states from the ground state $^6H_{5/2}$ are shown in Figure 6.

The optical absorption coefficient $\alpha(\lambda)$ were calculated using the Eq. 8, by taking the I_o as the intensity of the beam at the cell reference and I as the measured intensity of sample cell

$$\alpha(\lambda) = \frac{2.303\ \ln(I/I_0)_\lambda}{d} \qquad (8)$$

Where $(I/I_0)_\lambda = A$ is the absorbance and d is the sample thickness.

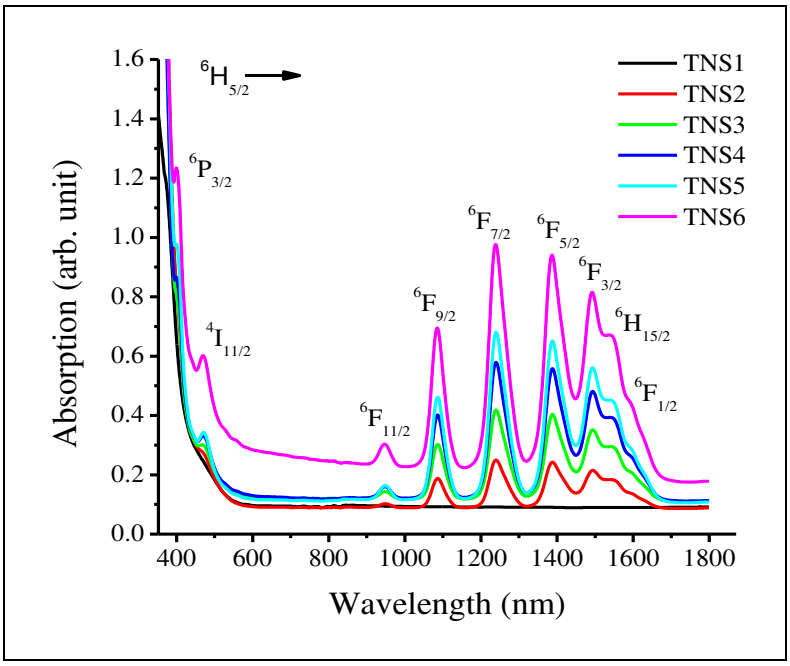


Figure 5: Normalized optical absorption spectra of glasses with different Sm_2O_3 mol%

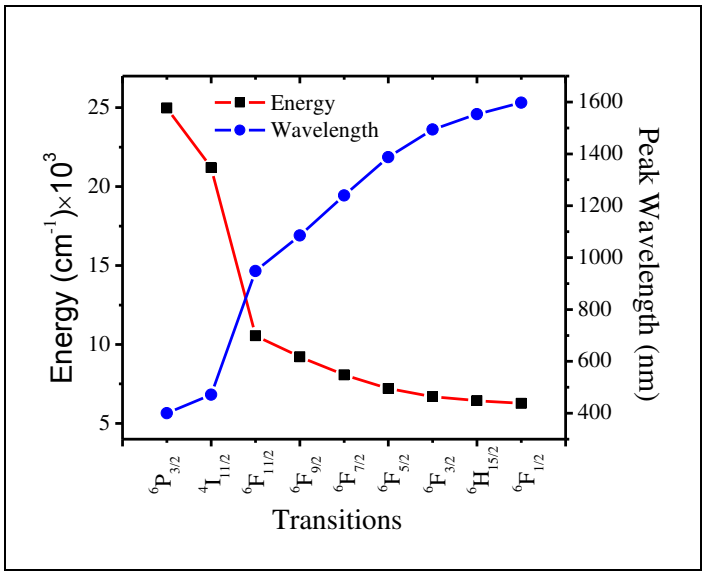
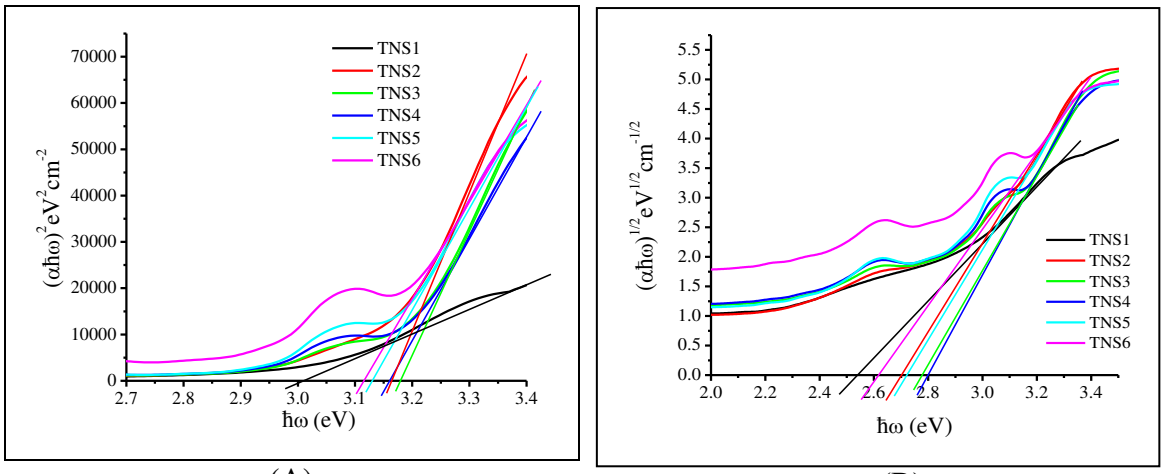


Figure 6: absorption pick wavelength and band transition for the excited states to the ground

The measured direct and indirect band gaps and Urbach band tail of different tellurite glasses are reported widely. In the crystalline or non-crystalline materials, there exist two kinds of band gap; direct band gap is the energy difference between valence band and conduction band with a conservative wave vector, while indirect band gap is determined due to bridging the gap between valence and conduction bands with contribution of lattice vibrations (phonons). Direct and indirect band gaps were first discussed by Davis and Mott [24] as,

$$\alpha(\omega) = B\frac{(\hbar\omega - E_{opt})^n}{\hbar\omega} \qquad (9)$$

Where α is the frequency (ω) dependent absorption, B is a constant and E_{opt} is the direct and indirect band gap. Direct (n=1/2) and indirect (n=2) optical band gaps are defined according to Al-Ani et al. [25]. It is found that most amorphous material best fit with n=2 gives reasonable fit to Eq. 9, representing the indirect allowed band transition [25]. Figure 7 shows the curves in determination of the direct and indirect band gap energies. The value of direct E_{dir} and indirect E_{in} band gap can be obtained by extrapolating the linear part of the $(\alpha\hbar\omega)^2$ versus phonon energy $(\hbar\omega)$ graph.



(A) (B)

Figure 7: (A) Typical plot of $(\alpha\hbar\omega)^2$ versus $(\hbar\omega)$ for (80-x) TeO_2-20Na_2O-xSm_2O_3, (B) Typical plot of $(\alpha\hbar\omega)^{1/2}$ versus $(\hbar\omega)$ for (80-x) TeO_2-20Na_2O-xSm_2O_3

The direct and indirect band gap energies values as a function of Sm2O3 concentration variation are illustrated in Figure 8. It can be noticed that indirect band energy increases with the increase of Sm^{3+}content from 0 to 1 mol% and it decreased for 1.2 and 1.5 mol%, this change in the band gap and energy is attributed to the variation of NBOs in the glass structure [14].

The Urbach energy (E_u) which is a character of disorder in the amorphous materials can be defined by a plot of natural logarithm of absorption coefficient $\alpha(\omega)$ as a function of photon energy ($h\omega$), and determining the inverse of its slope, as described by Eq. 10 [21]. A linear energy dependent density of states is suggested by Tauc *et al.* [26] at the band edges, E_c and E_v, where E_u=E_c-E_v is the band tail width, introduced by Urbach [21]:

$$\alpha(\omega) = B exp(\frac{\hbar\omega}{\Delta E}) \qquad (10)$$

Where, B is a constant and ΔE is the width of the band tail of the electron states. From Figure 9,

Urbach energy is determined from the slope of plot ln (α) versus $\hbar\omega$. The Urbach energy value for glass system was found to lie between 0.209 and 0.312 eV. According to Sreekanth *et al.*, the number of defects being a higher due to the increasing the Urbach energy [27]. Therefore, the decrease in the Urbach energy confirms that the numbers of defects are less. The obtained values are in the range of amorphous semiconductors between (0.046 and 0.66 eV) as reported by Davis and Mott [28].

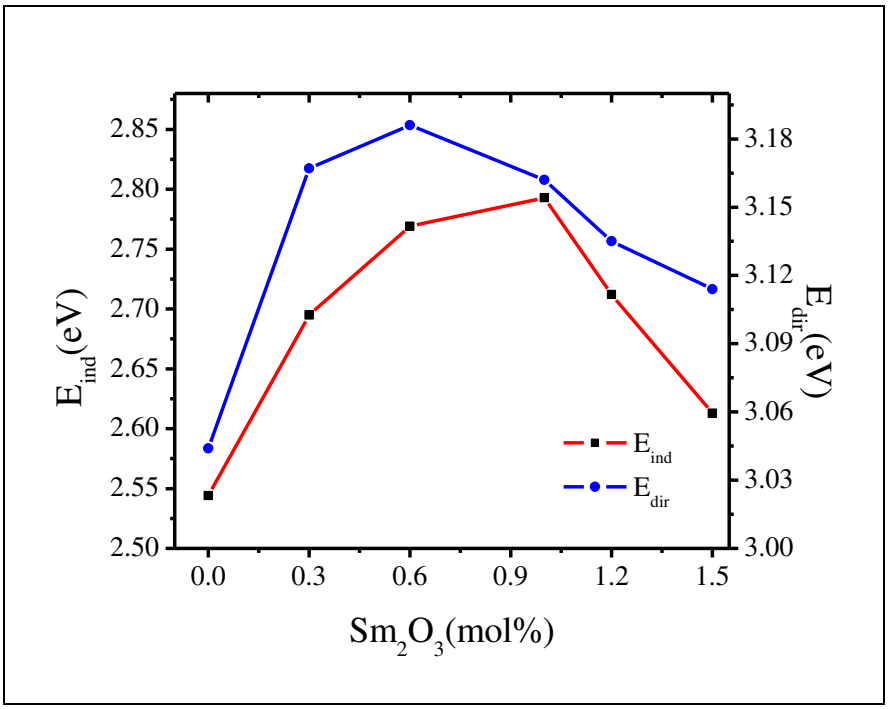


Figure 8: Direct and indirect band gap energies versus Sm_2O_3 concentration

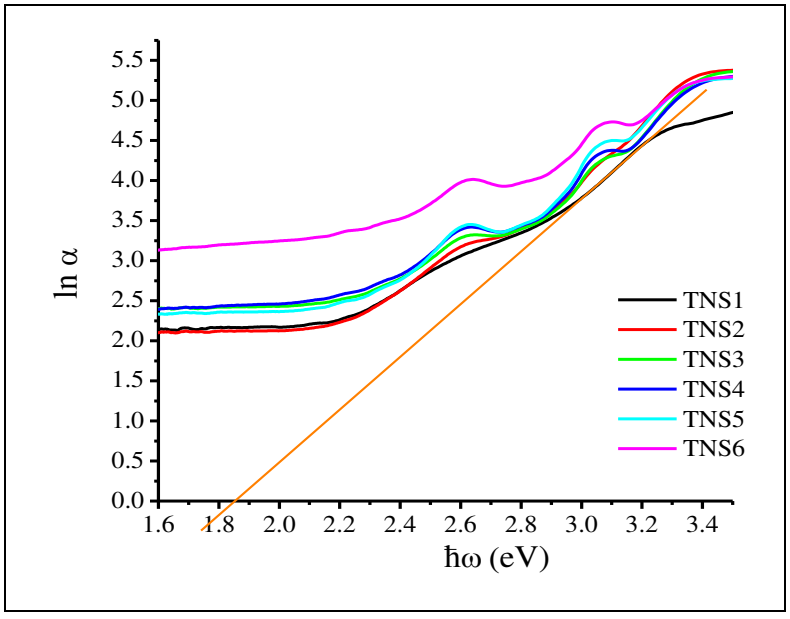


Figure 9: Plot of lnα versus $\hbar\omega$ for Urbach energy of (80-x) TeO_2-20Na_2O-$x$$Sm_2O_3$ glass system.

Figure 10 represents the behavior of direct band gap and Urbach energy of the samples with concentration of Sm_2O_3. The shifts of the absorption edge are almost likely related

to structural rearrangements of the glass network and modifier. The UV cut-off wavelength may be estimated from the absorption spectra, Figure 11 shows the optical absorption spectra for sample TNS1 and cut off wavelength versus sample code, direct band gap energy and cut off wavelength are listed in Table 3 in addition to Urbach energy.

Table 3: Direct band gaps E_{dir}, Urbach energy E_U and cut-off wavelength λ_c of the studied sodium tellurite glasses

Label	Glass Composition	E_{ind} [eV]	E_{dir} [eV]	E_u [eV]	λ_c [nm]
TNS1	$80TeO_2$-20Na2O	2.544	3.044	0.312	360.8
TNS2	$79.7TeO_2$-$20Na_2O$-$0.3Sm_2O_3$	2.695	3.167	0.256	363.11
TNS3	$79.4TeO_2$-$20Na_2O$-$0.6Sm_2O_3$	2.769	3.186	0.226	360.35
TNS4	$79TeO_2$-$20Na_2O$-$1Sm_2O_3$	2.793	3.162	0.217	361.32
TNS5	$78.8TeO_2$-$20Na_2O$-$1.2Sm_2O_3$	2.712	3.135	0.209	365.79
TNS6	$78.5TeO_2$-$20Na_2O$-$0.5Sm_2O_3$	2.613	3.114	0.309	366.15

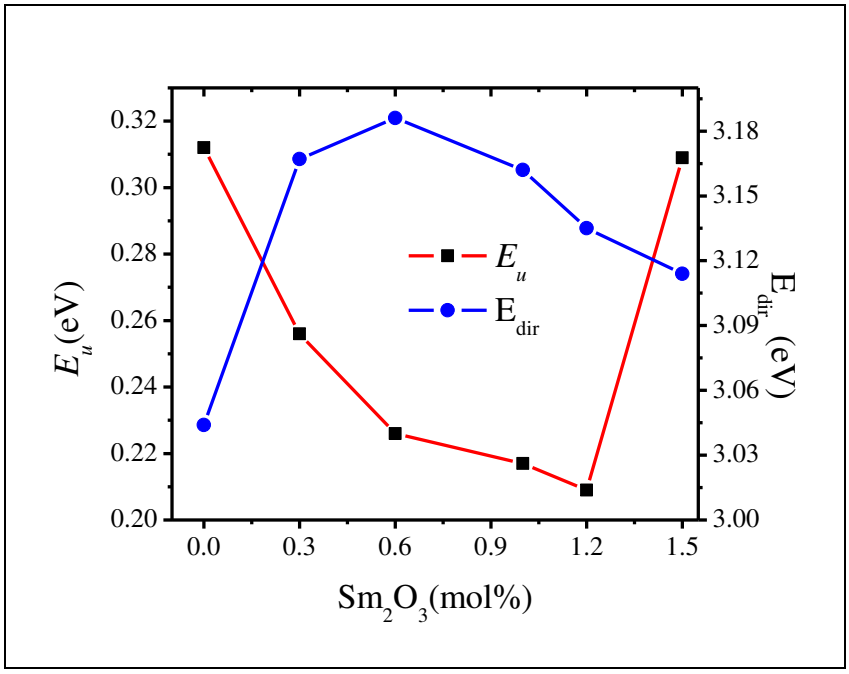


Figure 10: Direct band gap and Urbach energy versus Sm_2O_3 concentration

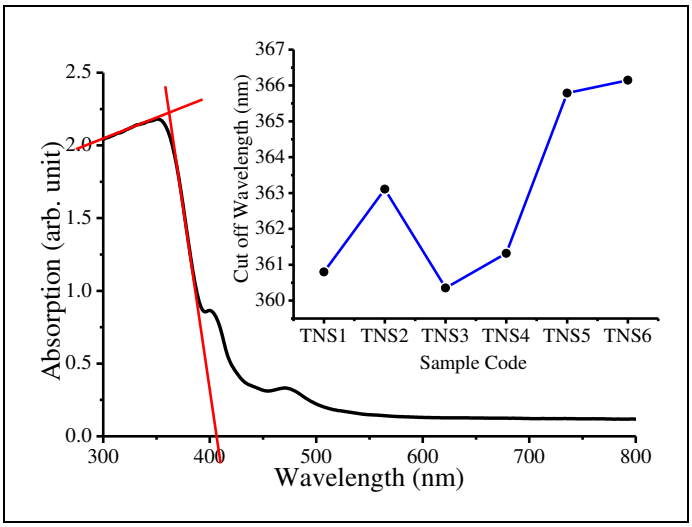


Figure 11: optical absorption spectra for sample TNS1 and cut off wavelength versus sample code

CONCLUSIONS

Series glass of Na_2O-TeO_2 with different mol% Sm_2O_3 concentration has been prepared by melt-quenching technique and the amorphous nature was confirmed by XRD. The Sm^{3+} ions concentration dependent variation in density, molar volume, refractive index, polarizability, band gap and Urbach energy are discussed and understood in terms of the formation of non-bridging oxygen. The optical absorption in UV-VIS-NIR region for Sm_2O_3 doped with TeO_2-Na_2O was measured at room temperature. The optical absorption spectra in the range of 200-1000 nm showed that the absorption edge was shifted to higher wavelength direction with the increasing of Sm_2O_3 concentration. We use Tauc/Mott-Davis Model to analyze the optical data for different composition ratio of (80-x) TeO_2-20Na_2O-xSm_2O_3 with concentration (x=0, 0.3, 0.6, 1, 1.2, 1.5). The direct transition for TNS are in between 3.044-3.186 eV, while for indirect transition from 2.544-2.793 eV. The band tail was calculated in exponential region and the value are obtained in range 0.209-0.312 eV. The role of Sm^{3+} ions in modifying the optical properties has been understood.

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