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Synthesis, Physical and Optical Properties of Titanium Doped Tellurium Oxide Glasses

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ABSTRACT

Titanium tellurite (TTN) glasses with the composition (90-x) %TeO2 –x% TiO2– 10%Na2O (where x varies 5 to 20% in the gap of 5%). Melt quenching was used to make them. These glass samples were studied using XRD at room temperature. The XRD signals corroborated the amorphous nature of the glass samples. The glass transition temperature of TTN4 glass was measured using differential scanning calorimetry (DSC), and the results demonstrate that as the TiO2 content of the glass increases, the glass's stability factor ΔT improves. Other characteristics of glass samples were computed, including density ρ, molar volume Vm, polaron radius Rp, oxygen packing density (OPD), intermolecular distance Ri and molar refraction Rm. In terms of the variation of TiO in the glass composition, the change in density and molar volume has been explored. The UV-VIS-IR spectra of samples were recorded in the 400nm to 1000nm spectral region, and the refractive index (n), absorption coefficient (α), direct and indirect forbidden energy band gaps (Eopt), and Urbach energy (Eu) were shown to decrease with TiO2 compositions.

Key Words: Tellurite glasses; Absorption Spectra; Structure analysis; Refractive index; Optical energy band gap; Urbach Energy.

I. INTRODUCTION

Tellurite glass systems were more appealing than oxide glass formers because of their low phonon energy (around 800 cm1), which increases the quantum efficiency from excited states of rare-earth ions in these matrix and allows for the implementation of efficient lasers and opticalamplifiers [1, 2]. These properties, due to the high polarisability of Te4+-ions (with a solitary electron pair 5s2), can be even more enhanced by means of the incorporation of other heavy metals oxides that can be easily polarised (e.g., Bi3+, Pb2+) or with empty d orbital (Ti4+, Nb5+). [3] Apart from these special optical properties, other advantages of such glasses are their good thermal and chemical stability, high rare earth ions solubility and high linear and nonlinear refractive indices, with a wide transmission window (typically 0.4–6 μm). The structure and optical properties of many kinds of tellurite glass have been studied, such as Te02 - Zn0[4], Te02-W03[5], Te02- K2O[6] and some ternary glass systems'" [7-8]. Other authors have enlarged the field of knowledge about tellurite glasses with research concerning ternary and quaternary systems.[9–13].

In this work, we report the synthesis, physical and optical properties of tellurite base glass of composition $TeO_2–TiO_2–Na_2O$ system. Afterwards, some of such glasses will be selected as the best for a further study focused on their application as photonic materials.

II. MATERIALS AND METHOD

Traditional melting and quench method has been implemented to prepare Titanium Oxide tellurite glass samples. High purity chemical substances (Otto) Tellurium oxide, Titanium Oxide and sodium oxid were taken in following composition:

I. TTN1≡85%TeO2-10%Na2O- 05%ZnO
II. TTN2≡80%TeO2-10% Na2O -10%ZnO
III. TTN3≡75%TeO2-10% Na2O -15%ZnO
IV. TTN4≡70%TeO2-10% Na2O -20%ZnO

For proper mixing mortar and pestle were used. Then the batch mixer was melted in alumina crucibles in a muffle furnace. Temperature was taken as high as 1100°Cto introduce molten vitreous property in it followed by physically stirring ensuring homogeneity in the mixture. It was further heated to 1200°Cfor 1 and ½ hour and then poured in stainless steel moulds to form pellets of diameter 10mm and thickness of 2 mm. For annealing a hot oven maintained at 250 °C was used for 60 minutes. X-RAY diffraction of sample glasses were studied for the endorsement of amorphous nature. Differential Scanning Calorimetry for the analysis of thermal properties. Absorption spectroscopy has been carried in the spectral range of 350 - 1000nm spectral range.

III. RESULTS AND DISCUSSION

3.1. Differential Scanning Calorimetry (DSC)

Titanium Tellurium Oxide the DSC curve of sampleTTN4 glass with 70%TeO2- 20%Ti2O3-10%Na2O chemical mixture is studied (Fig.1). It is possible to see the glass transition temperature Tg and the start crystallisation temperature Tc. In the temperature range of 30°C to 500°C, Differential Scanning Calorimetry is investigated. The scan clearly shows that the glass transition temperature Tg of synthesised ternary glass is mild at 320°C. The melting temperature Tm is 350 degrees Celsius, while the crystallisation temperature Tc is 470 degrees Celsius. The difference ΔT =Tc-Tg is commonly utilized as a key criterion for determining glass thermal stability [14]. It's worth noting that the higher the value of T, the greater the anti-crystallization ability. T of glasses is 150 degrees Celsius in our measurements, which is higher than that of glass tellurite glass (102 degrees Celsius) [15] and fluorophosphate glass (87 degrees Celsius) [16], but the modest value of T suggests that the thermal characteristics of glasses are unstable. However, if the T value is more than 100 degrees Celsius, the produced glass is stable and suitable for applications such as fiber and laser elements.

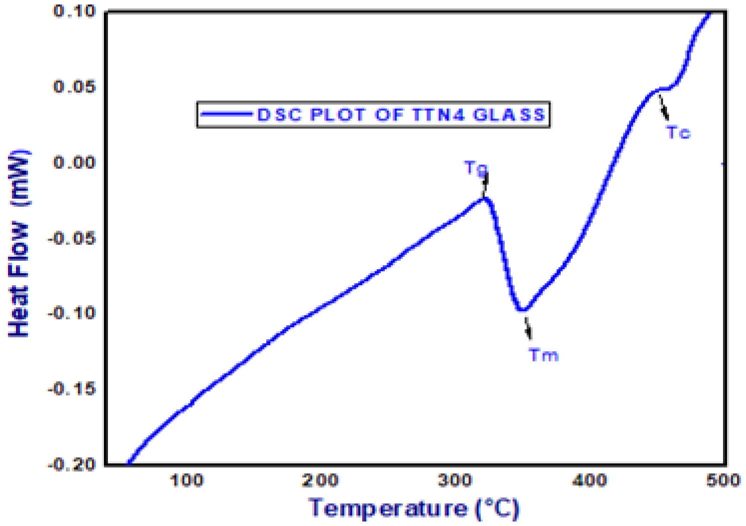

Fig. 1. DSC plot of TTN4 glass of composition 70%TeO2-20%Ti2O3-10%Na2O

3.2. Structure analysis

The representative powder XRD pattern of titanium -tellurite glasses of chemical compositions (90-x) %TeO2 –x% TiO2–10%Na2O (where x is 5, 10, 15 and 20%) are shown in Fig.2, justify the glassy natures of synthesized titanium- tellurite glasses. X-Ray differactogram is carried by Rigaku, Japan, Smart Lab 9kW at room temperature in the range of 10^{o} to 80^{o} value of 2θ. The diffractograms of the TTN samples contain a broad hump at near 30^{o}, and no other sharp spike were observed, which indicate the absence of crystallinity in samples .

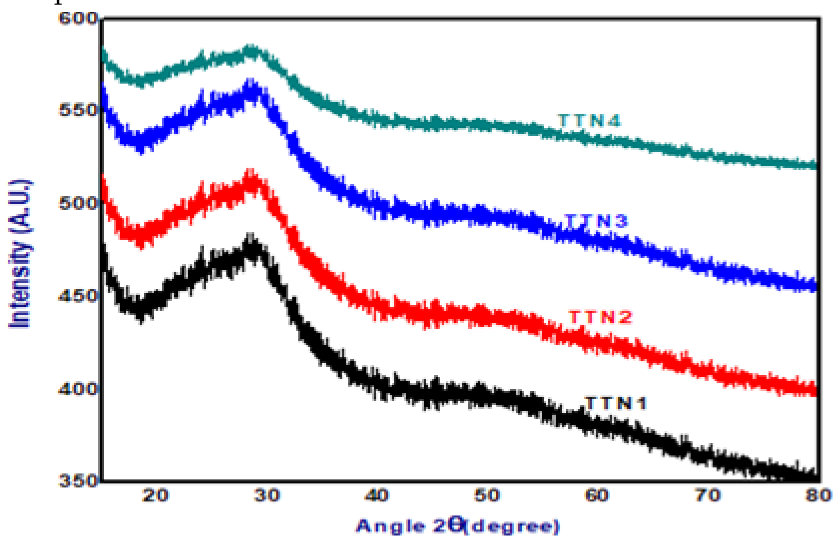

Fig.2.XRD plot for TTN glasses of chemical compositions (90-x)%TeO2 –x% TiO2– 10%Na2O

3.3. Physical Properties

The Archimedes principle was used to determine the densities (ρ) of produced ternary titanium tellurite glasses at room temperature. As a buoyant liquid, distilled water is employed. The glass samples TTN were weighed ωa in the air and ωl while dipped in a floating liquid (distilled water with a density of ρw = 1 g cm–3at ambient temperature). The following relationship was used to determine the densities of TTN glasses:

ρ = (ωa) ……. (1)

ωa−ωl

Figure 3 depicts the relationship between density and molar volume as a function of TiO concentration. The relationship between increasing density and decreasing molar volume is linear.

The molar volume (Vm) of TTN glasses was estimated using the following relation, with the help of computed densities and molecular weight

$Vm = M/\rho$ (2) …. (2)

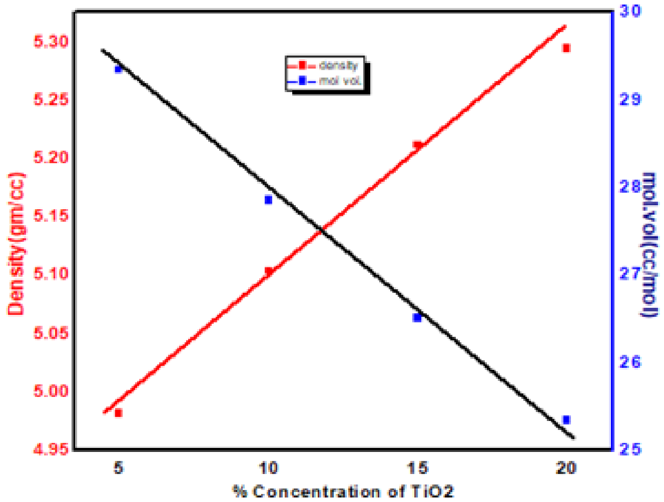

Fig. 3 Plot of variation of density and molar volume with varying TiO2 concentration

The oxygen packing density (OPD) of oxide glasses is a measure of the spatial layout of the oxide network. The oxygen packing density (OPD) is determined by the glass sample's molar volume (Vm) and the amount of oxygen atoms (n) accessible. The equation for determination of OPD is given as [17]

OPD = 1000×n

Vm……… (3)

By using the following relation the content of titanium ions in glass samples' N (ion/cm3) was estimated. [18]

N = mole% of **Ti** ions ×ρ×NA

Vm

… (4)

Where NA is Avogadro'snumber. Further the polaron radius (Rp), internuclear distance (Ri) and molar refraction (Rm),are calculated by using the ion concentration [19]

Rp = 1/2 (6πN) 1/3 (5)

Ri= (1/N) 1/3 (6)

Rm ={(n2-1)/n2+1)}× Vm (7)

Table 1 shows the computed values of physical attributes. With increasing TiO concentration, density values rose from 4.982 to 5.294 g/cm3. The average Ti-Ti distance, internuclear distance (Ri), Polaron radius (Rp), molar refraction (Rm) and Oxygen Packing density (OPD) were computed from density and molar volume measurements. When the concentration of TiO mole percent increases, the interionic distance (Ri), Polaron radius (Rp) and molar refraction (Rm) decrease.

Table 1. The physical attributes of TeO_2–TiO_2–Na_2O glass system

Name of the Sample	TTN1	TTN2	TTN3	TTN4
Batch composition in percent (TeO_2: TiO_2: Na_2O)	85:05:10	80:10:10	75:15:10	70:20:10
Molar Mass (M) gm/mol	146.2	142.2	138.2	134.2
ρ (g/cm^3)	4.982	5.104	5.212	5.294
V_m (cm^3/ mol)	29.345	27.860	26.516	25.349
OPD (mol/l)	68.153	71.786	75.427	78.897
N($\times 10^{23}$) (ions cm^{-3})	1.026	2.162	3.407	4.752
R_p (nm)	0.277	0.216	0.186	0.166
R_i (nm)	0.991	0.773	0.664	0.595
Rm(cm^3)	15.067	14.304	13.614	13.015

3.4. Absorption Spectra

UV-VIS-IR absorption spectra of ternary titanium tellurite glass samples have been taken in the wavelength range from 400nm to1000nm at room temperature are shown in Fig. 4. The absorption coefficient α is inversely depend on the thickness t of the sample and given by α = 2.302A/t [20], where A is the sample's absorbance.

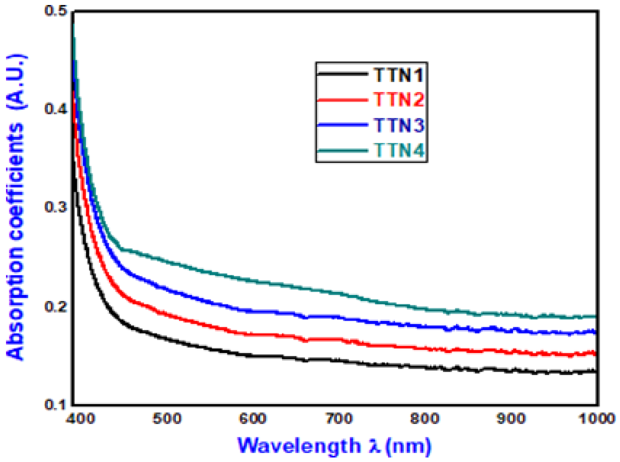

Fig. 4. Absorbance plot of TTN Glasses

3.4.1. Optical Energy Band Gap

In amorphous materials, it is well known that the absorption coefficient α depends on hν according to the following equation (7)

$\alpha\, hv = C(hv - Eg)\, m$ (7)

Where "C" stands for the proportionality constant, Eg for the optical band gap, and m for the transition process index. If m = 1/2, the allowable transition is direct, and if m = 2, the allowed transition is indirect. As a result, m = 1/2 has been used in equation(7) to compute the direct optical band gap in TTN glasses. Figure 5 depicts the curves of (αhν)2 versus incoming radiation energy " hν (in eV)" for synthesized TTN glasses. Extrapolating the linear component of the exhibited curves up to (αhν)2 = 0 yielded the optical band gap values. The value of Eg For the synthesized TTN1, TTN2, TTN3, and TTN4, glasses are found to be 3.15,3.12,3.10 and 3.08 eV.

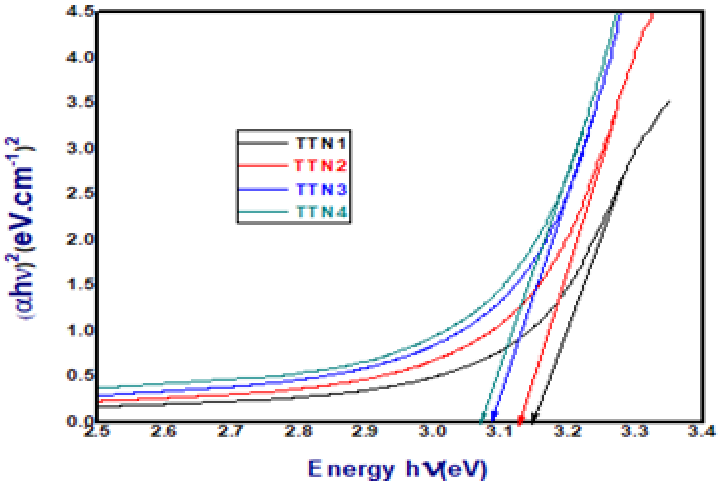

Fig. 5. Tauc's plots for direct band gap of TTN glasses

Indirect bandgap in Figure 6 shows the relationships between (αhν)1/2 and incoming radiation energy " hν (in eV)" for synthesized TTN glasses. Indirect optical band gap values calculated are 3.10, 3.05, 3.02, and 3.0 eV. As the TiO2 concentration increases, the values of the of optical band gaps decrease. This tendency may be explained in terms of structural changes occurring in glass systems [21].

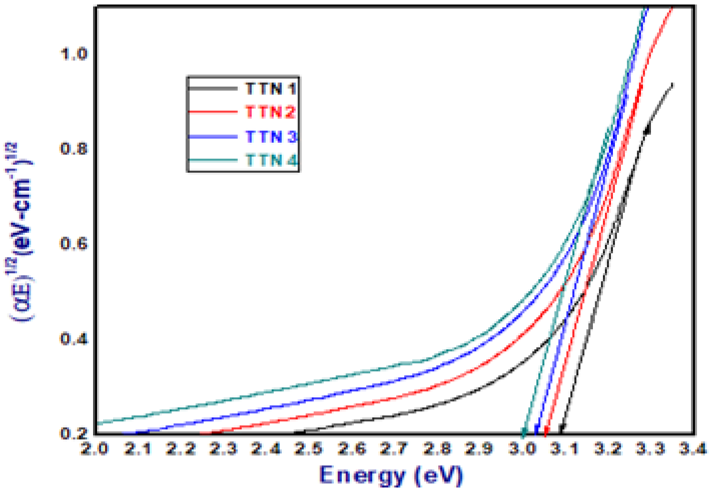

Fig. 6. Tauc's plots for indirect band gap of TTN glasses

3.4.2. Refractive index

The optical energy gap is dependent on the refractive index n.,and the optical energy gap Eg was investigated by the relationship (22)

$n2–1 = 1 – \sqrt{Eopt/20}$ ………. (8)

$n + 2$

The refractive index of TTN glasses rises with increasing in TiO2 concentration. In TTN glasses Titanium ions are present in the form of Ti4+ ions [23].

Variation of Eg and 'n' with increase in TiO2 concentration in glass network is shown in fig.7.

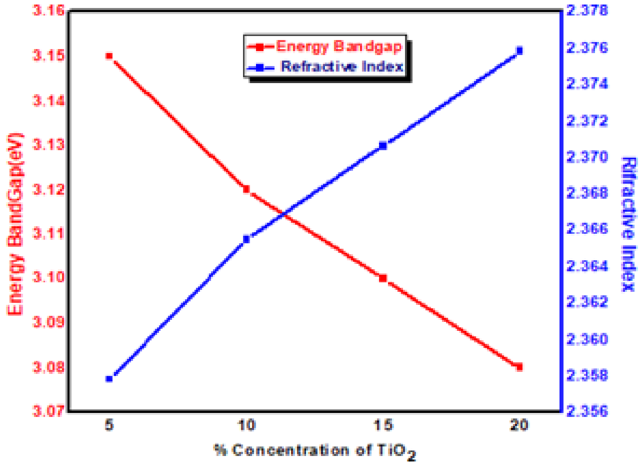

Fig.7. Variation of optical energy band gap and refractive index with TiO2 concentration

3.4.3. Urbach Energy

According to Urbach, in an amorphous material, the relation between the absorption coefficient and incident photon energy can be expressed as [24].

$\alpha = \alpha 0 ehv / Eu$ …… (9) where, α0 is proportionality constant Eq. (9) can be rewrite as

$ln\alpha = hv / Eu + consta$ …….(10)

The exponential behavior given in equation(9) has been demonstrated and the curves are plotted between logarithmic values of the absorption coefficient versus incident photon energy. The reciprocal of the slope of the linear portion of the curve between ln(α) versus hν (shown in Figure 8) provides the value of Urbach energy[25]. The values of Urbach energy of the prepared TTN samples are found 0.261, 0.212, 0.184 and 0.176 eV respectively.

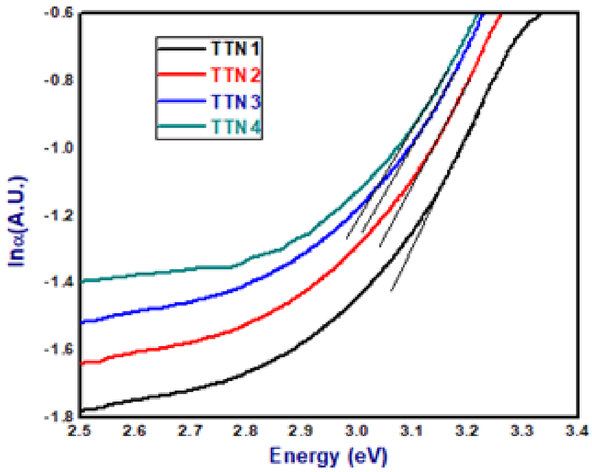

Fig. 8The Urbach's plot of synthesized TTN glasses

Table 2 Optical properties of ternaryxTiO-(90-x) TeO2 -10Na2O glasses

Glasses code	TTN1	TTN2	TTN3	TTN4
Direct energy band gap(eV)	3.15	3.12	3.10	3.08
Indirect energy band gap(eV)	3.10	3.05	3.02	3.0
Refractive index	2.357	2.365	2.370	2.375
Urbach energy (eV)	0.261	0.212	0.184	0.176

IV. DISCUSSION

The titanium tellurite glass systems of composition (90-x) %TeO2 –x% TiO2–10%Na2O (where x is 5, 10, 15 and 20%) were prepared successfully using conventional melt quenching method. Synthesized tellurite glasses having low transition temperature confirmed by DSC characterization and also the glass thermal stability ΔT =Tc–Tg . The XRD spectra confirmed the amorphous nature of synthesized glasses. Measured maximum refractive index and higher density are 2.375 and 5.294 g/cm3 respectively for TTN glasses. The OPD and ρ are found to increase with increasing TiO2 content. The expected decrease in the Rp and Ri with increasing concentration of TiO2 is observed. The optical absorption behavior of the samples is measured through UV–VIS-NIR spectroscopy. With increase of TiO2, optical bandgap decreases and refraction index increases. The maximum observed values of both the optical band gap and refractive index TTN glass samples are Eopt. = 3.15 eV (TiO2 -5%)and n=2.375 (TiO2 - 20%)respectively.

V. ACKNOWLEDGMENT

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