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Research Article

Influence of Eu^{3+} Concentration on the Structural and Physical Properties of Tellurite-Based Glasses

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Abstract

Eu^{3+}-doped sodium tungsten tellurite glasses of composition (79.5−x) TeO_2-10WO_3-10Na_2O-xEu_2O_3 (x = 0.5, 1.0 and 1.5 mol%), designated TNWEu (0.5), TNWEu (1.0) and TNWEu (1.5), were synthesized by the conventional melt-quenching technique to investigate the role of Eu^{3+} concentration in governing the structural, thermal and physical behaviour of the tellurite glass network. Differential scanning calorimetry of the base ternary glass revealed a glass transition temperature (Tg) of 320 ℃, a melting temperature of 350°C and a crystallization onset (Tc) of 470°C, yielding a thermal stability parameter ΔT (= Tc − Tg) of 150 ℃, which exceeds values reported for conventional tellurite (102 ℃) and fluorophosphate (87 ℃) glasses and indicates favourable resistance to devitrification. Physical parameters obtained from density and molecular weight showed systematic and monotonic trends with increasing Eu_2O_3 content: density increased from 4.546 to 4.662 g/cc while molar volume decreased from 34.840 to 34.660 cc/mol, Eu^{3+} ion concentration rose from 1.611 $\times 10^{20}$ to 4.848 $\times 10^{20}$ ions/cc, inter-nuclear distance and polaron radius decreased, field strength increased from 0.888 $\times 10^{14}$ to 1.854 $\times 10^{14}$ cm^{-2}, and oxygen packing density increased from 234.67 to 271.03 mol/l. These correlated trends indicate that Eu^{3+} ions progressively densify and cross-link the tellurite network, reducing free volume and non-bridging oxygen content as the dopant concentration increases. The combined structural compactness and thermal stability of the TNWEu glass system suggest its suitability as a host matrix for rare-earth-based photonic, optical amplification and solid-state lighting applications.

Keywords

Tellurite Glass, Europium (III) Doping, Rare-earth Ions, Glass Transition Temperature, Thermal Stability, Physical Properties, Oxygen Packing Density

1. Introduction

Tellurite-based glasses have attracted considerable scientific and technological interest due to their distinctive physical and optical properties compared with conventional silicate and borate systems. Glasses formed from Tellurium dioxide (TeO_2) are characterized by high refractive indices, wide infrared transmission windows, relatively low phonon energies

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(~750 cm^{-1}), and excellent rare-earth ion solubility, which make them particularly suitable for photonic device applications [1]. Their low melting temperatures and good glass-forming ability further enhance their practical advantages in material processing [2]. The reduced phonon energy of tellurite matrices suppresses multiphonon relaxation processes, thereby improving radiative efficiencies of embedded rare-earth ions compared to silica-based hosts [3]. Structural modification of tellurite glasses through the incorporation of network modifiers such as alkali and transition metal oxides plays a crucial role in tailoring their properties. The addition of Na_2O typically depolymerizes the Te-O-Te network by converting TeO_4 trigonal bipyramids into TeO_3 trigonal pyramids, generating non-bridging oxygens and altering the connectivity of the glass framework [4]. Meanwhile, WO_3 contributes to enhanced thermal stability and chemical durability, often participating in the glass network through W-O linkages that reinforce structural rigidity [5]. The balance between TeO_4 and TeO_3 structural units significantly influences density, molar volume, and thermal behavior, making compositional optimization essential for targeted applications [6].

Rare-earth doping has emerged as an effective strategy to introduce luminescent functionality into oxide glass systems. Among various rare-earth oxides, Europium (III) oxide (Eu_2O_3) is of particular importance because the Eu^{3+} ion exhibits sharp 4f-4f transitions and strong red emission, especially the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition [7]. This transition is highly sensitive to the local symmetry and covalency of the surrounding environment, making Eu^{3+} ions effective structural probes in glass matrices [8]. Consequently, Eu^{3+}-doped tellurite glasses have been extensively investigated for applications in solid-state lighting, display technologies, and optical amplifiers [9]. The incorporation of Eu^{3+} ions into tellurite glass networks can induce structural rearrangements and influence both physical and thermal parameters. Depending on concentration and host composition, Eu^{3+} ions may act as network modifiers, altering bond angles and oxygen coordination, which in turn affects glass transition temperature (Tg), crystallization resistance, and density [10]. Variations in europium content can also modify oxygen packing density and molar volume, reflecting changes in network compactness and connectivity [11]. Understanding these compositional effects is critical for correlating microscopic structural evolution with macroscopic thermal stability and optical performance.

Although numerous studies have examined rare-earth-doped tellurite systems, systematic investigations correlating europium concentration with structural, thermal, and physical properties within multicomponent TeO_2-Na_2O-WO_3 glasses remain relatively limited [12]. Therefore, a comprehensive study combining structural analysis, thermal characterization, and physical property evaluation is necessary to elucidate the role of Eu^{3+} ions in modifying the tellurite glass matrix. Such insights are essential for the rational design of advanced photonic materials with tunable properties for emerging optoelectronic applications [13].

2. Experimentation

The chemical composition of the Eu3+ doped tellurite glass is (80-x)%TeO2+10%Na2O+10%WO3+x%Eu2O3. Four different values of x corresponding to Eu2O3 concentrations of 0.5, 1 and 1.5 mol% are used in our studies. The corresponding samples are called TNWEu (0.5), TNWEu (1.0) and TNWEu (1.5). Samples with a reported purity of 99.9% were used of Otto chemie Pvt. Ltd. Calculated quantities of the chemical components were mixed in an agate mortar and melted in an electric furnace at 900 ℃ for 50 to 55 minutes in alumina crucibles so that a homogeneously mixed melt was obtained. The glass samples were subsequently annealed at 200 ℃ for 1hour, after that slowly cooled down to room temperature. The annealing process sought to minimize the internal mechanical stress and obtain glasses with good mechanical stability. The DSC scans of as-cast glass specimens were carried out in the TA Instruments, USA. X-ray diffraction (XRD) patterns were carried out at room temperature in a Bruker Model No. D2 Phaser 2nd Gen.

3. Characterization

3.1. XRD

Figure 1 shows the XRD patterns of TNWEu nanostructures at Eu concentrations of 0.5, 1.0, and 1.5 mol%. All three samples display only a broad, diffuse hump around $2\theta \approx 25–30°$ with no sharp Bragg peaks, indicating an amorphous or poorly crystalline structure. The peak position and shape remain nearly unchanged across all Eu concentrations, suggesting that Eu doping does not induce any new crystalline phase or significant structural change in the host matrix.

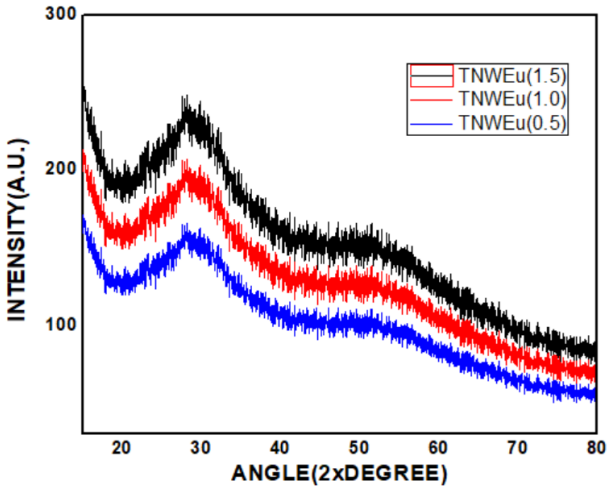

Figure 1. *shows the X-ray diffraction (XRD) patterns of TNWEu Glasses.*

3.2. DSC

The DSC curve of Eu3+ doped tellurite glass sampleTNWEu (1.5) is studied (Figure 2). It is possible to see the glass transition temperature Tg and the start crystallisation temperature Tc. In the temperature range of 30 ℃ to 500 ℃, Differential Scanning Calorimetry is investigated. The scan clearly shows that the glass transition temperature Tg of synthesised ternary glass is mild at 320 ℃. 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.

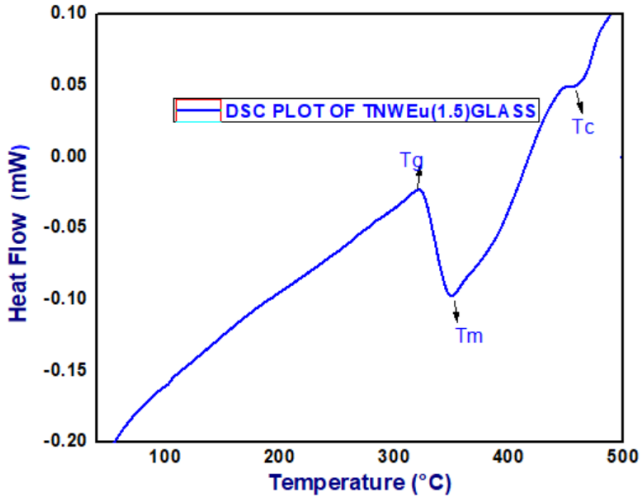

Figure 2. *shows the DSC curve of TNWEu (1.5) Glass.*

4. Physical Parameters

The physical characteristics of an oxide glass system provide fundamental insight into the manner in which the glass network reorganizes itself upon the incorporation of a dopant ion. In the present work, sodium tungsten tellurite glasses of composition (79.5−x) TeO_2-10WO_3-10Na_2O-xEu_2O_3 (x = 0.5, 1.0 and 1.5 mol%), designated as TNWEu (0.5), TNWEu (1.0) and TNWEu (1.5), were prepared by the conventional melt-quenching technique, and their density (ρ), molar volume (V_m), europium ion concentration (N), inter-nuclear distance (R_i), polaron radius (R_p), field strength (F) and oxygen packing density (OPD) were evaluated from the measured density and molecular weight using standard formulae reported in the literature [17-19]. These parameters, together, describe the compactness of the glass network, the strength of interaction between the dopant Eu^{3+} ion and its surrounding oxide ligands, and the extent of structural connectivity of the tellurite network, and they are widely used to correlate the physical structure of a glass with its optical and spectroscopic behaviour [20, 21].

4.1. Density and Molar Volume

The density (ρ) of a glass is one of the most sensitive indicators of structural compactness, since it depends on the type of coordination polyhedra, the geometrical configuration of the network, the cross-link density, the atomic mass and the interstitial free space of the constituent atoms/ions [17, 19]. The molar volume (V_m), calculated from the density and the average molecular weight (M) of the glass as $V_m = M/\rho$, is a more direct measure of the compactness of the glass network than density alone, because it accounts for changes in molecular weight arising from substitution of one oxide by another [17, 22]. In the present glasses, the systematic replacement of TeO_2 by Eu_2O_3 changes both the average molecular weight and the packing of the glass-forming units, and the resulting variation of ρ and V_m with Eu_2O_3 content is generally interpreted in terms of the difference in ionic radius and field strength between the host cation (Te^{4+}) and the dopant rare-earth cation (Eu^{3+}), and in terms of the creation or elimination of non-bridging oxygens (NBOs) within the tellurite network [22-24].

4.2. Rare-Earth Ion Concentration (N)

The concentration of Eu^{3+} ions per unit volume (N), expressed in ions/cc, was calculated using the relation [17, 18].

$$N = (\rho \times N_A \times \text{mol\% of } Eu_2O_3 \times n) / M$$

where N_A is Avogadro's number (6.023×10^{23} mol^{-1}), n is the number of dopant cations per formula unit and M is the molecular weight of the glass. Physically, N represents the number density of the optically/structurally active dopant ion, and it increases monotonically with the Eu_2O_3 content because a larger fraction of the glass-forming oxide is progressively substituted by the rare-earth oxide; a similar trend has been reported for other rare-earth doped oxide glass systems [25]. The ion concentration N is the key quantity from which the two other structural parameters discussed below, namely the inter-nuclear distance and the polaron radius, are derived.

4.3. Inter-Nuclear Distance (Ri) and Polaron Radius (Rp)

The mean inter-nuclear (inter-ionic) separation between neighbouring Eu^{3+} ions, R_i, was obtained from the ion concentration using the expression proposed by Dimitrov and co-

workers [17-19].

$$R_i = (1/N)^{1/3}$$

while the polaron radius, R_p, which represents the radius of the smallest sphere that contains the volume associated with one dopant ion and describes the extent to which the electronic charge of the Eu^{3+} ion is localized around its lattice site, was evaluated from [17-19].

$$R_p = (1/2)\ (\pi/6N)^{1/3}$$

Both R_i and R_p decrease with increasing Eu_2O_3 content, which is a direct consequence of the increase in N; a shorter separation between neighbouring rare-earth ions is generally associated with a tighter and more cross-linked glass network and with an enhanced probability of ion-ion interaction and non-radiative energy transfer (e.g. cross-relaxation and concentration quenching) among Eu^{3+} ions at higher dopant levels [25, 26].

4.4. Field Strength (F)

The field strength (F) of the Eu^{3+} ion, which quantifies the strength of the electrostatic field exerted by the dopant cation at its immediate coordination shell, was calculated from the polaron radius using the relation [17, 18].

$$F = z / R_p^2$$

where z is the valency of the dopant ion (z = 3 for Eu^{3+}). Since F is inversely proportional to the square of R_p, it increases with increasing Eu_2O_3 concentration, reflecting a progressively stronger local electric field and a more ionic, tightly bound Eu-O environment as the average separation between rare-earth ions is reduced. A rise in field strength with dopant concentration has been reported for several rare-earth doped tellurite, borate and phosphate glass systems and is generally correlated with the increase in the covalent/ionic character of the metal-oxygen bond and with modifications in the ligand field around the rare-earth ion [25, 26].

4.5. Oxygen Packing Density (OPD)

The oxygen packing density (OPD), expressed in mol/l, is a measure of the tightness of packing of oxygen atoms within the three-dimensional glass network and was calculated using the relation [17, 18].

$$OPD = 1000 \times \rho \times n_O / M$$

where n_O is the number of oxygen atoms in the formula unit and M is the molecular weight of the glass. A higher OPD value indicates a more closely packed, rigid glass network with fewer interstitial voids, whereas a lower OPD is associated with a more open network structure containing a larger fraction of non-bridging oxygens. Because OPD depends directly on ρ/V_m, its compositional trend generally mirrors that of density and is inversely related to the trend observed for molar volume. Taken together, the variation of ρ, V_m, N, R_i, R_p, F and OPD with Eu_2O_3 content, summarized in Table 1.

Table 1. *TNWEu glasses physical characteristics.*

Specimen	TNWEu (0.5)	TNWEu (1.0)	TNWEu (1.5)
Batch Composition	79.5%TeO_2-10%WO_3-10%NaO_2-0.5%Eu_2O_3	79%TeO_2-10%WO_3-10%NaO_2-1.0%Eu_2O_3	78.5%TeO_2-10%WO_3-10%NaO_2- 1.5%Eu_2O_3
Molar Mass M - ($g.mol^{-1}$)	158.38	159.15	160.34
Molar Volume V_m-($cc.mol^{-1}$)	34.840	34.711	34.660
Density ρ (gm/cc)	4.546	4.585	4.662
W ion concentration (N)($\times 10^{20}$/cc)	1.611	3.043	4.848
inter-nuclear distance (Ri)- x 10^{-7} cm	1.837	1.486	1272
polaron radius (Rp)- x 10^{-8} cm	5.134	4.153	3.553
field strength (F)(x 10^{14} cm^{-2})	0.888	1.357	1.854
OPD (mol/l)	234.67	265.50	2.71.03

5. Conclusion

Sodium tungsten tellurite glasses of composition (79.5−x) TeO_2-10WO_3-10Na_2O-xEu_2O_3 (x = 0.5, 1.0 and 1.5 mol%) were successfully prepared by the melt-quenching route, and the influence of Eu^{3+} concentration on their thermal and physical characteristics was systematically evaluated. DSC analysis of the ternary tellurite host confirmed a well-defined glass transition (Tg ≈ 320°C) and a thermal stability parameter ΔT of 150 ℃, higher than that reported for conventional tellurite and fluorophosphate glasses, confirming adequate resistance against crystallization for device processing such as fiber drawing. With increasing Eu_2O_3 content from 0.5 to 1.5 mol%, the density and oxygen packing density of the glasses increased steadily while the molar volume, inter-nuclear distance and polaron radius decreased, and both the Eu^{3+} ion concentration and field strength increased monotonically. These correlated variations demonstrate that Eu^{3+} ions are progressively incorporated into the tellurite network as network-modifying/cross-linking species, promoting a more compact and rigid glass structure with a shorter average separation between rare-earth ions at higher doping levels. The combination of enhanced structural compactness, increasing field strength and satisfactory thermal stability indicates that the TNWEu glass series, particularly the higher-Eu_2O_3 compositions, is a promising host for Eu^{3+}-based luminescent and photonic applications, including solid-state lighting, display phosphors and optical amplifiers. Future work correlating these structural and thermal trends with the optical absorption and photoluminescence behaviour of the $^5D_0 \rightarrow {}^7F_2$ transition would further establish the structure-property relationships needed for the rational design of Eu^{3+}-doped tellurite-based optical materials.

Abbreviations

Ri	Inter-Nuclear Distance
Rp	Polaron Radius
F	Field Strength
OPD	Oxigen Packing Density

Author Contributions

Akanksha Tiwari: Conceptualization, Data curation, Investigation, Methodology, Writing – original draft

Preeti Chincholikar: Formal Analysis, Investigation, Writing – review & editing

Sandeep Kumar Sharma: Resources, Validation, Writing – review & editing

Ghizal Firdous Ansari: Conceptualization, Project administration, Supervision, Writing – review & editing

Conflicts of Interest

The authors declare no conflict of interest.

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