

RESEARCH ARTICLE

Microhardness and FTIR Spectroscopic Analysis of Oxy–Tellurite Glass Doped with Tm_2O_3

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ABSTRACT: An oxy-tellurite glass system with the composition $60\text{TeO}_2\text{-}10\text{BaF}_2\text{-}10\text{ZnO-}10\text{Nb}_2\text{O}_5\text{-}5\text{Bi}_2\text{O}_3\text{-}5\text{TiO}_2$ was successfully synthesized using the conventional melt quenching technique. Four distinct glass samples were prepared with varying concentrations of Tm_2O_3 dopant, specifically 0, 10^4 , 3×10^4 , and 4×10^4 ppm. The structural characteristics of these prepared glass specimens were comprehensively investigated through Fourier-transform infrared spectroscopy, while the mechanical properties were evaluated using Vickers microhardness measurements. The microhardness analysis revealed a systematic enhancement in Vickers hardness values from 3.1 to 3.3 GPa as the Tm_2O_3 concentration increased from 0 to 4×10^4 ppm, indicating progressive structural densification within the glass network. FTIR spectroscopic analysis confirmed the presence of characteristic vibrational modes inherent to tellurite-based glass networks, including TeO_4 trigonal bipyramidal units, TeO_{3+1} polyhedral structures, and TeO_3 trigonal pyramidal configurations. Additionally, vibrational bands corresponding to Zn–O, Nb–O, and O–H stretching modes were identified within the spectral range. Notably, the concentration of residual hydroxyl ions exhibited a significant increase from 1.10 to 3.23×10^{19} ions/cm³ with rising Tm_2O_3 content, which is attributed to alterations in the fluorine substitution equilibrium induced by the presence of BaF_2 in the glass matrix. The observed structural modifications and enhanced mechanical properties suggest that the incorporation of Tm_2O_3 effectively compacts the glass network through increased cross-link density and improved rigidity. These findings provide valuable insights into the structure-property relationships governing rare-earth-doped tellurite glasses for potential photonic applications.

Keywords: Tellurite glass, Fluoride ions, FTIR spectroscopy, Thulium oxide, Microhardness, Heavy metal oxides

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1. INTRODUCTION

Tellurium oxide (TeO_2) occupies a unique position among glass-forming materials, as it does not inherently vitrify when melted alone but readily forms stable glasses upon the introduction of appropriate modifying oxides [1]. This distinctive behavior stems from the asymmetric coordination environment of tellurium atoms, which possess a lone pair of electrons that facilitates the formation of various structural units including TeO_4 trigonal bipyramids, TeO_{3+1} polyhedra, and TeO_3 trigonal pyramids. The resulting TeO_2 -based

glasses exhibit remarkably superior infrared transmission characteristics when compared to their silicate counterparts, a property attributable to the larger atomic size and substantially greater mass of tellurium relative to silicon. This enhanced infrared transparency, extending beyond $5 \mu\text{m}$, makes tellurite glasses particularly attractive for applications requiring extended wavelength coverage in the mid-infrared spectral region, including thermal imaging, infrared sensing, and optical communications.

The glass-forming ability of TeO_2 with various oxide types has been extensively investigated across numerous composition systems incorporating R_2O , RO , R_2O_3 , RO_2 , and RO_3 oxides [2-4]. These comprehensive studies have established the glass formation regions within the TeO_2 -oxide phase diagrams and documented various physical and chemical characteristics essential for practical applications. Among the various tellurite glass compositions, those

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containing heavy metal oxides such as ZnO , Nb_2O_5 , Bi_2O_3 , and TiO_2 have demonstrated exceptional stability against devitrification, combined with favorable optical and mechanical properties. The inclusion of halides such as BaF_2 further enhances these materials by reducing hydroxyl ion contamination and improving rare-earth ion solubility through the modification of the local ligand field around dopant ions. The resulting oxy-fluoride tellurite glasses represent a class of materials that successfully combines the low phonon energy characteristics of tellurite networks with the reduced hydroxyl content provided by fluoride incorporation.

The technological relevance of rare-earth-doped tellurite glasses has been significantly amplified by the growing demand for compact and efficient laser sources operating near $2.0\ \mu\text{m}$. Such laser systems find diverse applications across multiple domains including remote atmospheric sensing, coherent laser radar systems for wind detection, minimally invasive medical surgical procedures, precise materials processing, and ultra-low-loss long-span optical communications [5-8]. The trivalent thulium ion has emerged as a particularly attractive active dopant for these applications because its $^3\text{F}_4 \rightarrow ^3\text{H}_6$ electronic transition generates radiation centered around $2.0\ \mu\text{m}$ with favorable spectroscopic characteristics. Several compelling factors account for the extensive research attention devoted to Tm^{3+} -doped laser materials in recent years [9]. First, the strong absorption band of Tm^{3+} located around $800\ \text{nm}$ exhibits excellent spectral overlap with the emission band of commercially available high-power AlGaAs laser diodes, enabling efficient optical pumping with well-established pump sources. Second, theoretical quantum efficiency approaching 200% can be achieved in Tm^{3+} -doped systems at high doping concentrations due to the efficient cross-relaxation process ($^3\text{H}_6, ^3\text{H}_4 \rightarrow ^3\text{F}_4, ^3\text{F}_4$), which effectively multiplies the number of photons generated per pump photon absorbed. Third, the emission range of Tm^{3+} -doped fiber lasers can be continuously tuned over an exceptionally wide spectral interval, providing flexibility in addressing different application requirements through appropriate cavity design.

The pursuit of efficient Tm^{3+} -doped $2.0\ \mu\text{m}$ optical fiber lasers necessitates careful consideration of several host glass properties that critically influence laser performance. Among these factors, the phonon energy distribution of the host matrix plays a decisive role in determining the non-radiative relaxation rates between excited energy levels, with lower phonon energies generally reducing multi-phonon decay and enhancing radiative quantum efficiency. Environmental durability ensures long-term device reliability under various operating conditions, while favorable fiber-drawing ability enables the fabrication of low-loss optical fibers from the glass preforms. The solubility of rare-earth ions within the host matrix determines the maximum achievable dopant concentration without concentration quenching effects, which is particularly important for Tm^{3+} systems where the cross-relaxation efficiency depends sensitively on ion-ion separation. The purity of starting materials directly impacts the presence of undesirable background impurities such as

transition metal ions or hydroxyl groups that can introduce additional non-radiative decay channels and reduce laser efficiency.

Various glass hosts have been successfully employed for Tm^{3+} -doped $2\ \mu\text{m}$ fiber lasers, including silica glasses, fluoride glasses, and more recently tellurite glasses [5, 6, 10-13]. Silica-based fibers offer the advantage of well-established manufacturing processes and robust mechanical properties, though their higher phonon energies limit the achievable quantum efficiency. Fluoride glasses provide substantially lower phonon energies and reduced non-radiative decay rates, but their mechanical strength and chemical durability often present challenges for practical device deployment. Tellurite glasses offer an attractive compromise, combining phonon energies intermediate between silica and fluoride systems with excellent rare-earth ion solubility, favorable mechanical properties, and resistance to moisture attack. The unique combination of low phonon energy, high linear and nonlinear refractive indices, and broad infrared transparency makes tellurite glasses exceptionally well-suited for rare-earth-doped fiber laser applications operating in the $2\ \mu\text{m}$ spectral region.

The novelty of the present study lies in the systematic investigation of the combined effects of Tm_2O_3 doping on both the structural characteristics and mechanical properties of the oxy-fluoride tellurite glass system $60\text{TeO}_2\text{-}10\text{BaF}_2\text{-}10\text{ZnO-}10\text{Nb}_2\text{O}_5\text{-}5\text{Bi}_2\text{O}_3\text{-}5\text{TiO}_2$. While previous investigations have separately examined the spectroscopic properties of Tm^{3+} in various tellurite hosts or the microhardness behavior of rare-earth-doped tellurite glasses, a comprehensive correlation between structural evolution and mechanical response as a function of Tm_2O_3 concentration in this specific multi-oxide composition has remained unexplored. This work uniquely bridges the gap between structural characterization through FTIR spectroscopy and mechanical property assessment through Vickers microhardness measurements, providing fundamental insights into the structure-property relationships governing rare-earth-doped tellurite glasses. The integration of BaF_2 in the composition offers the additional advantage of reducing hydroxyl contamination while simultaneously modifying the glass network connectivity, and the systematic variation of Tm_2O_3 concentration enables the elucidation of dopant-induced structural changes that influence both the mechanical integrity and optical performance of these promising materials.

In this paper, we report a comprehensive investigation of the microhardness and structural characteristics of oxy-tellurite glasses within the composition $60\text{TeO}_2\text{-}10\text{BaF}_2\text{-}10\text{ZnO-}10\text{Nb}_2\text{O}_5\text{-}5\text{Bi}_2\text{O}_3\text{-}5\text{TiO}_2$ doped with varying concentrations of Tm_2O_3 . The glass samples were synthesized using the conventional melt quenching technique, and their structural features were thoroughly examined through Fourier-transform infrared spectroscopy. Vickers microhardness measurements were employed to evaluate the mechanical properties and their evolution with increasing rare-earth oxide content. The correlations between structural modifications observed in the FTIR spectra and the

corresponding changes in microhardness values are systematically analyzed to understand the role of Tm_2O_3 incorporation in modifying the glass network architecture and mechanical resilience. The influence of BaF_2 on the hydroxyl ion concentration and its implications for the structural integrity of the glass network are also discussed in detail.

2. EXPERIMENTAL DETAILS

2.1. Glass Synthesis and Preparation

The glass samples investigated in this study were prepared according to the nominal composition $60\text{TeO}_2\text{-}10\text{BaF}_2\text{-}10\text{ZnO-}10\text{Nb}_2\text{O}_5\text{-}5\text{Bi}_2\text{O}_3\text{-}5\text{TiO}_2\text{-}x\text{Tm}_2\text{O}_3$ (in mol%), where x represents the Tm_2O_3 doping concentration with values of 0, 10^4 , 3×10^4 , and 4×10^4 ppm. The starting materials employed for the synthesis consisted of high-purity reagent grade chemicals, including TeO_2 (99.99%), BaF_2 (99.99%), ZnO (99.99%), Nb_2O_5 (99.99%), Bi_2O_3 (99.99%), TiO_2 (99.99%), and Tm_2O_3 (99.99%). These raw materials were carefully weighed according to their respective stoichiometric proportions using an analytical balance with precision of ± 0.0001 g. The weighed powders were thoroughly mixed and homogenized in an agate mortar for approximately 60 minutes to ensure uniform distribution of all constituent oxides and fluoride compounds. The resulting homogeneous powder mixtures were then transferred into high-purity platinum crucibles, which were selected due to their resistance to corrosion and chemical reactivity with the tellurite melt.

The melting process was conducted in an electric resistance furnace equipped with a temperature controller capable of maintaining the desired temperature within $\pm 5^\circ\text{C}$ accuracy. The powder mixtures were heated to 990°C at a ramp rate of 10°C per minute and maintained at this temperature for 90 minutes under a continuous flow of dry oxygen gas to prevent any possible oxidation reactions and to facilitate the removal of volatile impurities. The dry oxygen atmosphere was maintained throughout the melting process at a flow rate of approximately 2 L per minute. After the melting period, the glass melts were rapidly poured onto preheated graphite molds maintained at room temperature.

The casting process was performed quickly to avoid any premature crystallization and to ensure the formation of homogeneous amorphous samples. Following casting, the glass specimens were immediately transferred to an annealing furnace preheated to 330°C , where they were kept for 2 hours to relieve internal thermal stresses generated during the rapid cooling process. The annealed glass samples were then allowed to cool gradually to room temperature at a rate of approximately 1°C per minute. The prepared glass samples were designated as Sample A (undoped), Sample B (10^4 ppm Tm_2O_3), Sample C (3×10^4 ppm Tm_2O_3), and Sample D (4×10^4 ppm Tm_2O_3), with their detailed compositions presented in Table 1.

Following the annealing procedure, the glass samples were subjected to a systematic polishing process to achieve optically flat surfaces suitable for spectroscopic investigations and mechanical property measurements. The polishing process involved sequential grinding with progressively finer grades of silicon carbide abrasive papers, starting from 400 grit and progressing through 600, 800, 1000, and 1200 grit. Final polishing was accomplished using diamond paste with particle sizes of $3\text{ }\mu\text{m}$ and subsequently $1\text{ }\mu\text{m}$, applied on a rotating polishing wheel. The polished glass samples were cleaned ultrasonically in acetone for 10 minutes followed by distilled water rinsing and drying in an oven at 100°C for 30 minutes to remove any surface contamination or residual polishing compounds.

2.2. Vickers Microhardness Measurements

The Vickers microhardness measurements were conducted at ambient room temperature in air using a standard microhardness testing apparatus equipped with a diamond pyramid indenter having a square base and pyramidal angle of 136° between opposite faces. The indentation tests were performed on the polished surfaces of all glass samples under an applied load of 5 gf (grams-force), which corresponds to approximately 0.049 N. A holding time of 15 seconds was maintained for each indentation to ensure complete elastic recovery and to standardize the measurement conditions. The indentation load was carefully selected to produce well-defined indentation marks with diagonal lengths suitable for accurate measurement while avoiding excessive cracking or fracture of the brittle glass specimens.

Table 1. Composition of Tm_2O_3 -doped glass systems

Sample ID	Glass Composition (mol%)
Sample A	$60\text{TeO}_2\text{-}10\text{BaF}_2\text{-}10\text{ZnO-}10\text{Nb}_2\text{O}_5\text{-}5\text{Bi}_2\text{O}_3\text{-}5\text{TiO}_2$
Sample B	$60\text{TeO}_2\text{-}10\text{BaF}_2\text{-}10\text{ZnO-}10\text{Nb}_2\text{O}_5\text{-}5\text{Bi}_2\text{O}_3\text{-}5\text{TiO}_2\text{-}10^4\text{ ppm Tm}_2\text{O}_3$
Sample C	$60\text{TeO}_2\text{-}10\text{BaF}_2\text{-}10\text{ZnO-}10\text{Nb}_2\text{O}_5\text{-}5\text{Bi}_2\text{O}_3\text{-}5\text{TiO}_2\text{-}3 \times 10^4\text{ ppm Tm}_2\text{O}_3$
Sample D	$60\text{TeO}_2\text{-}10\text{BaF}_2\text{-}10\text{ZnO-}10\text{Nb}_2\text{O}_5\text{-}5\text{Bi}_2\text{O}_3\text{-}5\text{TiO}_2\text{-}4 \times 10^4\text{ ppm Tm}_2\text{O}_3$

For each glass sample, a minimum of five indentations were made at distinctly separated locations to avoid any mutual interference of stress fields. The diagonal lengths of each indentation, designated as d_1 and d_2 , were measured immediately after unloading using an optical microscope attached to the microhardness tester with a calibrated micrometer eyepiece having a precision of $\pm 0.5 \mu\text{m}$. The average diagonal length d was calculated as the arithmetic mean of d_1 and d_2 . The Vickers hardness number (HV) was then determined using the standard equation (1):

$$HV = \frac{2F \sin \frac{136^\circ}{2}}{d^2} \quad (1)$$

Where, F represents the applied load expressed in Newtons and d denotes the arithmetic mean of the two diagonal lengths measured in millimeters. The values obtained for the five indentations were averaged, and the standard deviation was calculated to assess the measurement reproducibility. Samples exhibiting microcracking or irregular indentation geometry were excluded from the analysis, and additional indentations were performed to maintain statistical significance.

3. RESULTS AND DISCUSSION

3.1. Vickers Microhardness Analysis

The Vickers microhardness measurements conducted on the prepared glass samples revealed a systematic enhancement in mechanical properties with increasing Tm₂O₃ content. Figure 1 illustrates the variation of Vickers hardness values as a function of Tm₂O₃ doping concentration, demonstrating a clear increasing trend from 3.1 to 3.3 GPa as the dopant concentration rises from 0 to 4×10^4 ppm. The corresponding numerical data, including the individual diagonal length measurements and calculated hardness values for all samples, are presented in Table 2. This observed improvement in microhardness indicates that the incorporation of thulium ions into the tellurite glass network induces substantial

structural modifications that enhance the material's resistance to plastic deformation.

The microhardness parameter fundamentally represents the magnitude of stress required to eliminate the free volume present within the glass structure. This free volume can be conceptualized as the degree of openness or compactness inherent to the amorphous atomic arrangement, which directly influences the mechanical response of the material [14-16]. In the present system, the progressive addition of Tm₂O₃ appears to promote structural densification through the formation of additional cross-linking bonds within the glass network. The observed increase in hardness from 3.1 to 3.3 GPa suggests that the thulium ions participate actively in network modification, leading to a more constrained atomic configuration with reduced interstitial spaces.

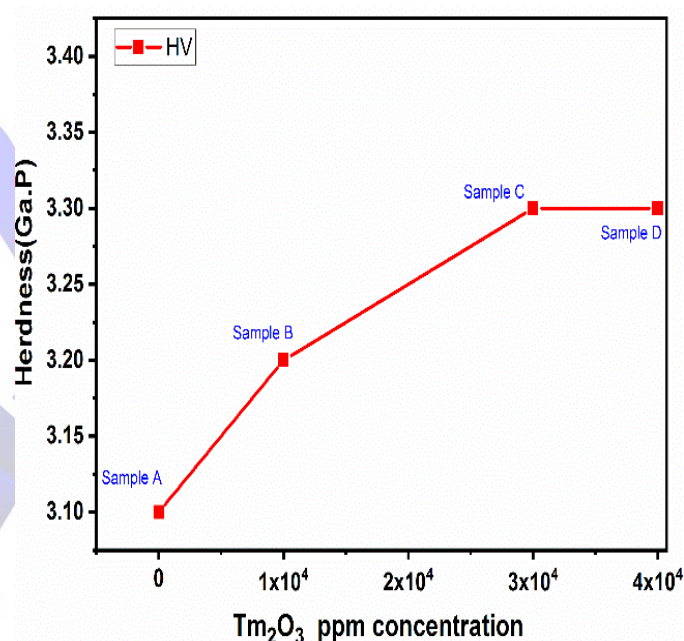


Fig. 1. Variation of Vickers microhardness (HV) with Tm₂O₃ doping concentration for the prepared oxy-telluride glass system.

Table 2. Vickers microhardness measurement results for the prepared glass samples doped with Tm₂O₃.

Sample Code	d_1 ($\times 10^{-3}$ mm)	d_2 ($\times 10^{-3}$ mm)	d^2 ($\times 10^{-6}$ mm ²)	HV (GPa)	Chemical Composition
A	17.0	17.0	289.0	3.1	60TeO ₂ -10BaF ₂ -10ZnO-10Nb ₂ O ₅ -5Bi ₂ O ₃ -5TiO ₂
B	17.2	16.6	285.6	3.2	60TeO ₂ -10BaF ₂ -10ZnO-10Nb ₂ O ₅ -5Bi ₂ O ₃ -5TiO ₂ -10 ⁴ ppm Tm ₂ O ₃
C	16.4	16.4	268.9	3.3	60TeO ₂ -10BaF ₂ -10ZnO-10Nb ₂ O ₅ -5Bi ₂ O ₃ -5TiO ₂ -3 × 10 ⁴ ppm Tm ₂ O ₃
D	17.3	15.5	268.9	3.3	60TeO ₂ -10BaF ₂ -10ZnO-10Nb ₂ O ₅ -5Bi ₂ O ₃ -5TiO ₂ -4 × 10 ⁴ ppm Tm ₂ O ₃

The structural mechanism underlying this hardness enhancement can be understood by considering the role of Tm_2O_3 in modifying the tellurite glass network. When thulium oxide is introduced into the glass composition, the Tm^{3+} ions are expected to occupy interstitial positions within the tellurite network or substitute for Te^{4+} ions, depending on the local coordination environment. This incorporation creates additional bonding opportunities through the formation of Tm-O-Te linkages, which effectively increase the cross-link density of the glass network. The higher cross-link density translates directly into improved mechanical stiffness and enhanced resistance to indentation-induced deformation. Furthermore, the presence of Tm^{3+} ions with their relatively high field strength may attract surrounding oxygen atoms, thereby locally compressing the glass structure and contributing to the overall densification.

It is noteworthy that the increase in microhardness from 3.1 to 3.3 GPa, while modest in absolute magnitude, represents a significant improvement given the relatively low Tm_2O_3 concentrations employed in this study. The dopant levels ranging from 0 to 4×10^4 ppm correspond to only 0 to 0.004 mol% Tm_2O_3 , yet the observed hardness enhancement demonstrates the effectiveness of even trace amounts of rare-earth oxide in modifying the mechanical properties of tellurite glasses. This sensitivity to dopant concentration highlights the important role that rare-earth ions play in altering the local structure and bonding characteristics of the glass network.

For comparative purposes, it is instructive to examine the microhardness behavior of related tellurite glass systems reported in the literature. In the composition $75\text{TeO}_2\text{-}10\text{Nb}_2\text{O}_5\text{-}10\text{ZnO-}5\text{PbO}$, the Vickers hardness was found to increase from 2.34 to 3.93 GPa with increasing Er_2O_3 concentration from 0 to 8750 ppm [16]. This significantly larger hardness enhancement observed in the erbium-doped system compared to the present Tm_2O_3 -doped glasses may be attributed to differences in the base glass composition, the ionic radius and field strength of the respective rare-earth ions, and the concentration ranges employed. The comparison nonetheless confirms that rare-earth oxide doping generally promotes mechanical reinforcement in tellurite glass networks through similar structural densification mechanisms.

Analyses of microhardness behavior in glass materials provide valuable insights into the amorphous structure, where elastic parameters are intimately correlated with lattice configuration and interatomic bonding forces. The microhardness technique serves as an effective probe for investigating the interaction between modifier and former networks, revealing important information about glass microstructure and the distribution of structural units [16-18]. The Vickers microhardness instrument offers particular advantages for elucidating the components of glassy materials due to its sensitivity, reliability, and cost-effectiveness. This methodology provides an effective tool for analyzing both opaque and transparent glass specimens to examine glass production quality, mechanical stiffness, structural stability, and microstructural variations. The

indentation technique's ability to probe local mechanical properties makes it especially valuable for studying composition-structure-property relationships in complex multi-component glass systems.

3.2. FTIR Spectroscopic Analysis

3.2.1. Hydroxyl Ion Concentration

The infrared transmission spectra of the Tm^{3+} -doped glass samples are presented in Figure 2, revealing several characteristic absorption bands that provide comprehensive information about the structural building units present within the glass network. The absorption band observed in the 2500-3700 cm^{-1} spectral region is attributed to stretching vibrations of free hydroxyl groups incorporated into the glass structure [2]. The band centered at approximately 3000 cm^{-1} was specifically utilized to estimate the residual hydroxyl ion concentration using equation (2), with the corresponding absorption coefficient calculated from equation (3) [3,4].

$$N_{OH} = \frac{A_v}{\epsilon_{OH} L} \ln\left(\frac{1}{T_r}\right) \quad (2)$$

Where: A_v is Avogadro's number, L is the glass sample thickness, ϵ_{OH} is the molar absorptivity of free OH^- groups. As no relevant value of ϵ_{OH} has yet been reported for tellurite glasses but we use the value $\epsilon_{OH} = 49.1 \times 10^3 \text{ cm}^2/\text{mol}$ determined in silicate glasses [3]. The glass absorption coefficient nearly at 3000 cm^{-1} can be calculated from the transmission spectra as follows:

$$\alpha_{OH} = \frac{\ln(1/T_r)}{L} \quad (3)$$

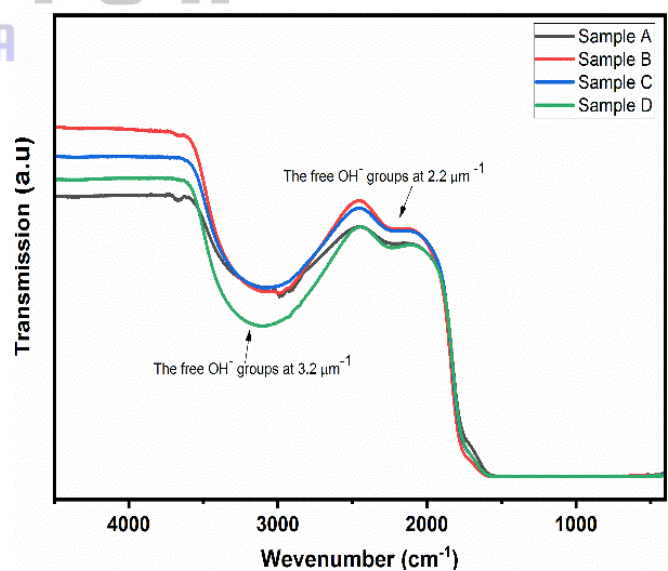


Fig. 2. Infrared transmission spectra of the prepared Tm^{3+} -doped tellurite glasses in the 2500-3700 cm^{-1} region showing the hydroxyl absorption band.

Table 3. Residual hydroxyl ion concentration (N_{OH}) for the prepared glass samples as a function of Tm_2O_3 doping concentration.

Sample Code	Tm_2O_3 Concentration (ppm)	$N_{\text{OH}} (\times 10^{19} \text{ ions/cm}^3)$
A	0	1.10
B	10^4	1.85
C	3×10^4	2.61
D	4×10^4	3.23

The residual hydroxyl ion concentration (N_{OH}) was found to increase systematically from 1.10×10^{19} to 3.23×10^{19} ions/ cm^3 with increasing Tm_2O_3 content from 0 to 4×10^4 ppm. This observed increase in N_{OH} with rising Tm_2O_3 concentration can be rationalized by considering the fluorine substitution equilibrium in the glass melt. The introduction of BaF_2 into the glass composition generally facilitates the replacement of hydroxyl ions by fluorine atoms through the chemical reaction $[\text{OH}^- + \text{F}^- \rightarrow \text{HF} + \text{O}^{2-}]$, which effectively scavenges hydroxyl species from the melt during the melting process [3, 5]. However, the presence of increasing concentrations of Tm_2O_3 appears to shift this equilibrium, possibly through competitive coordination of fluorine atoms by Tm^{3+} ions or by altering the local basicity of the melt, thereby reducing the efficiency of hydroxyl removal.

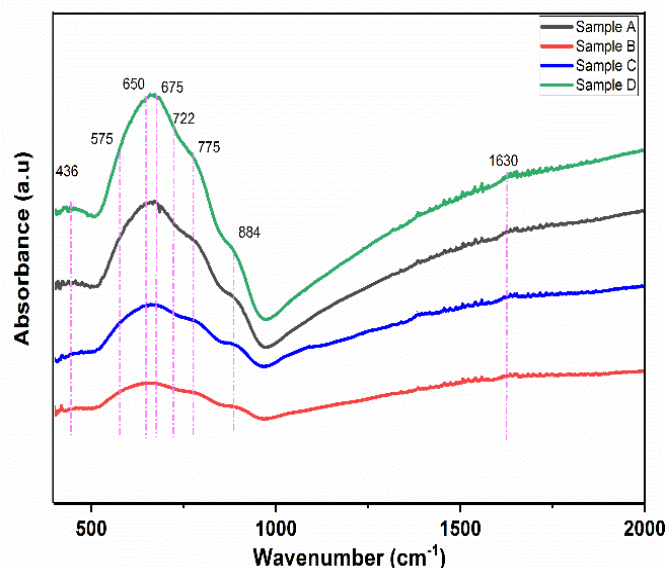
The N_{OH} values obtained in the present study compare favorably with those reported for various tellurite and related glass systems. For the composition $15\text{BaO}-10\text{Ga}_2\text{O}_3-70\text{GeO}_2-4\text{La}_2\text{O}_3-1\text{Tm}_2\text{O}_3$ (mol%), an N_{OH} value of 9.08×10^{19} ions/ cm^3 has been reported [1, 19, 20], which is substantially higher than the values obtained in this work. This difference likely arises from the presence of BaF_2 in the present composition, which effectively reduces hydroxyl contamination through the fluorine substitution mechanism. For the glass system $85\text{TeO}_2-5.0\text{Nb}_2\text{O}_5-5.0\text{ZnO}-5.0\text{LiF}$, a significantly lower value of 5.16×10^{18} ions/ cm^3 was observed [4], demonstrating the effectiveness of fluoride incorporation in minimizing hydroxyl concentration. In the related system $\text{TeO}_2\text{-BaO-BaF}_2\text{-Nb}_2\text{O}_5$ doped with rare-earth ions, N_{OH} values decreased from 5.24×10^{19} to 2.88×10^{19} ions/ cm^3 with increasing dopant concentration [5, 21], exhibiting a trend similar to that observed in the present work.

The presence of hydroxyl ions in glass materials is of considerable importance because OH^- groups introduce additional phonon modes that can contribute to non-radiative relaxation of excited rare-earth ions, thereby reducing the quantum efficiency of luminescence. The relatively low N_{OH} values achieved in the present glasses, particularly when compared to fluoride-free tellurite systems, suggest that these materials are promising candidates for photonic applications requiring efficient rare-earth luminescence.

3.2.2. Network Structural Units

The FTIR vibrational bands serve as characteristic fingerprints of the various structural building units present within the prepared glass network. The complete FTIR spectra of the glass system are illustrated in Figure 3, revealing distinct absorption features corresponding to different polyhedral configurations. The detailed band assignments based on literature comparisons are summarized in Table 4 [6-20]. A systematic analysis of these absorption bands provides valuable insights into the structural modifications induced by Tm_2O_3 doping.

The first set of absorption bands observed in the 436-470 cm^{-1} spectral range is attributed to symmetric stretching vibrations of Zn-O bonds in ZnO_4 tetrahedral units, confirming the incorporation of ZnO into the network-forming region [6, 7]. These bands may additionally arise from the vibrations of various building units such as BiO_n and ZnO_n polyhedra, reflecting the complex nature of the multi-component glass network. The symmetric vibrations of Te-O-Te bridges connecting different tellurite complexes also contribute to this spectral region. The persistence of these bands with increasing Tm_2O_3 concentration suggests that the basic zinc-containing structural units remain largely unaffected by the doping process.

**Fig. 3.** FTIR absorption spectra of the prepared oxy-tellurite glass system with varying Tm_2O_3 concentrations (0, 10^4 , 3×10^4 , and 4×10^4 ppm).

The absorption bands appearing in the 575-602 cm^{-1} range are associated with vibrations of the continuous glass network composed of TeO_4 trigonal bipyramidal units [8]. These bands serve as indicators of network connectivity and provide information about the degree of polymerization within the tellurite glass structure. The presence of well-defined bands in this region confirms the formation of the characteristic tellurite network structure. The bands observed in the 650-664 cm^{-1} range are assigned to symmetrical vibrations of Te-O_{ax} bonds in TeO_4 tetrahedral units [9, 10],

with the intensity of these bands showing a systematic increase and shifting toward higher wavenumbers with increasing Tm_2O_3 content. This spectral evolution suggests that the incorporation of thulium ions promotes the formation of additional TeO_4 units and enhances the rigidity of the tellurite network.

The absorption bands in the $666-675\text{ cm}^{-1}$ region correspond to stretching vibrations of tellurium atoms bonded to bridging oxygen atoms in TeO_3 and TeO_{3+1} units [11]. These bands are particularly informative regarding the degree of network connectivity, as bridging oxygen atoms contribute to the three-dimensional network structure. The bands observed in the $703-722\text{ cm}^{-1}$ range are attributed to stretching modes of non-bridging oxygen atoms present in TeO_{3+1} and TeO_3 units [12, 13]. The simultaneous presence of both bridging and non-bridging oxygen-related bands indicates that the glass network contains a mixture of different tellurite structural units, with the relative proportions influenced by the composition and thermal history.

The absorption bands in the $775-791\text{ cm}^{-1}$ range are assigned to the symmetric and asymmetric vibrational modes of $Te_{eq}-O$ bonds in TeO_{3+1} trigonal pyramid units or TeO_3 polyhedral configurations [14, 15]. These bands provide additional evidence for the presence of lower-coordination tellurite units in the glass network. The bands appearing in the $884-926\text{ cm}^{-1}$ region are attributed to stretching vibrations of Nb-O bonds in NbO_6 octahedral units [16]. The observed shift of these bands toward higher wavenumbers with increasing Tm_2O_3 content may indicate deformation of the NbO_6 units, suggesting that the incorporation of thulium ions influences not only the tellurite network but also the coordination environment of niobium atoms.

The spectral features observed in the present study are consistent with those reported for related glass systems. The composition $75TeO_2-10ZnO-(10-x)Nb_2O_5-5Li_2O-xCe_2O_3$ (where $x = 0.5, 1, 1.5, 2, 2.5\text{ mol\%}$) exhibited similar

vibrational bands corresponding to TeO_4 and NbO_6 units [17]. The $TeO_2-Nb_2O_5-TiO_2$ glass system also showed comparable spectral features [18], as did the $TiO_2-TeO_2-ZnO-Bi_2O_3-Nb_2O_5$ composition [19]. The two bands observed around $1630-1637\text{ cm}^{-1}$ demonstrate the bending vibration of absorbed water and surface hydroxyl groups, as well as the O-H stretching mode in the glass structure [20]. These bands are characteristic of surface contamination and confirm the presence of some residual moisture on the glass surfaces despite the careful preparation procedures.

The structural evolution observed in the FTIR spectra with increasing Tm_2O_3 concentration indicates that the thulium ions actively participate in modifying the glass network architecture. The systematic shifts in band positions and variations in band intensities suggest that the incorporation of Tm^{3+} ions promotes the conversion of non-bridging oxygen units to bridging oxygen units, thereby increasing network connectivity and enhancing the overall structural rigidity [21, 22]. This structural densification mechanism is entirely consistent with the microhardness enhancement observed in the same glass samples, confirming the direct correlation between structural modifications at the molecular level and the macroscopic mechanical properties of the glass material.

The comprehensive FTIR analysis reveals that the present oxy-tellurite glass system possesses a complex network structure comprising multiple coordination units including TeO_4 trigonal bipyramids, TeO_{3+1} polyhedra, TeO_3 trigonal pyramids, ZnO_4 tetrahedra, NbO_6 octahedra, and BiO_n polyhedra. The distribution of these structural units is influenced by the composition and particularly by the Tm_2O_3 doping concentration. The balanced presence of both bridging and non-bridging oxygen units contributes to the excellent glass-forming ability of this composition, while the incorporation of fluoride through BaF_2 provides additional benefits in terms of reducing hydroxyl contamination and modifying the network structure.

Table 4. FTIR absorption band assignments for the $60TeO_2-10BaF_2-10ZnO-10Nb_2O_5-5Bi_2O_3-5TiO_2-xTm_2O_3$ glass system.

Absorption Band (cm^{-1})	Band Assignment
436-470	Symmetric stretching vibrations of Zn-O in ZnO_4 tetrahedral units; vibrations of BiO_n and ZnO_n polyhedra; symmetric Te-O-Te bridge vibrations [6,7]
575-602	Vibrations of continuous network composed of TeO_4 trigonal bipyramidal units [8]
650-664	Symmetrical vibrations of $Te-O_{ax}$ bonds in TeO_4 tetrahedral units (tbp) [9,10]
666-675	Stretching vibrations of tellurium with bridging oxygen in TeO_3/TeO_{3+1} units [11]
703-722	Stretching modes of non-bridging oxygen in TeO_{3+1} and TeO_3 units [12,13]
775-791	($Te_{eq}-O$) symmetric and asymmetric vibrational modes of TeO_{3+1} polyhedral or TeO_3 trigonal pyramid units [14,15]
884-926	Stretching vibrations of Nb-O bonds in NbO_6 units; possible contribution from TeO_{3+1}/TeO_3 units [16-19]
1630-1637	Bending vibration of absorbed water and surface hydroxyl groups; O-H stretching modes [20]

4. CONCLUSION

The oxy-tellurite glass system with composition 60TeO_2 - 10BaF_2 - 10ZnO - $10\text{Nb}_2\text{O}_5$ - $5\text{Bi}_2\text{O}_3$ - 5TiO_2 doped with varying concentrations of Tm_2O_3 was successfully synthesized using the conventional melt quenching technique. The structural characteristics and mechanical properties of the prepared glasses were systematically investigated through FTIR spectroscopy and Vickers microhardness measurements. The microhardness analysis revealed a progressive increase in Vickers hardness values from 3.1 to 3.3 GPa with increasing Tm_2O_3 concentration from 0 to 4×10^4 ppm, indicating significant structural densification and enhanced network rigidity resulting from the incorporation of thulium ions. The FTIR spectroscopic analysis confirmed the presence of characteristic vibrational modes corresponding to various structural units including TeO_4 trigonal bipyramids, TeO_{3+1} polyhedra, TeO_3 trigonal pyramids, ZnO_4 tetrahedra, and NbO_6 octahedra. The residual hydroxyl ion concentration was found to increase from 1.10 to 3.23×10^{19} ions/ cm^3 with increasing Tm_2O_3 content, which is attributed to alterations in the fluorine substitution equilibrium induced by the presence of BaF_2 in the glass matrix. The systematic shifts in band positions and variations in band intensities observed in the FTIR spectra suggest that Tm^{3+} ions promote the conversion of non-bridging oxygen units to bridging oxygen units, thereby increasing network connectivity. The strong correlation between structural modifications at the molecular level and the macroscopic mechanical properties confirms that Tm_2O_3 doping effectively compacts the tellurite glass network through increased cross-link density and improved structural rigidity, making these materials promising candidates for photonic applications requiring both favorable optical characteristics and enhanced mechanical robustness.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

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Availability of data and material

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Authors' contributions

Y.M. AbouDeif: Formal Analysis, Data Curation, interpretation of results and Original draft preparation; W. H. Salem: Sample preparation, Experimental Work, Data collection, and interpretation of results.

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