
TELLURITE AND HEAVY-METAL-OXIDE TELLURITE GLASSES: A REVIEW OF STRUCTURE, PROPERTIES, PROCESSING AND EMERGING APPLICATIONS

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ABSTRACT

Tellurite glasses occupy an important position among oxide glasses because their structural chemistry permits substantial compositional modification while retaining useful optical, thermal, spectroscopic and radiation-interaction characteristics. The classical development of tellurite-glass science began with the structural studies of TeO₂ glass by Barady, followed by investigations of glass formation and network connectivity. These studies established that the local structure of tellurite glass can retain important features of the parent TeO₂ crystal even though long-range crystalline order is lost [1–3]. Subsequent work demonstrated that modifiers and heavy-metal oxides can alter Te–O coordination, network connectivity and physical properties, thereby expanding the range of functional tellurite compositions [4–6]. More recent studies have investigated ZnO-, Er₂O₃-, Sm₂O₃-, PbO-, Nb₂O₅-, rare-earth- and Ag-containing systems for optical, thermal, radiation-shielding, nonlinear and laser applications [6–22]. In particular, rare-earth-doped tellurite glasses have attracted sustained interest because of their infrared emission and suitability as gain media. Nd³⁺-doped tellurite fibres and microspheres have demonstrated laser operation, while Ag-containing systems provide routes for modifying luminescence through local-field and energy-transfer effects [23–37]. This review summarizes the structural foundations of tellurite glasses, the role of composition and modifiers, recent developments in heavy-metal-oxide tellurite systems, and the progression toward photonic, laser, radiation-shielding, electronic and nanostructured applications.

KEYWORDS: Tellurite glass; TeO₂; heavy-metal oxides; glass structure; rare-earth ions; Nd³⁺; Er³⁺; PbTe; optical properties; laser glass; microspheres; radiation shielding.

1. INTRODUCTION

Tellurite glasses are oxide glasses in which TeO₂ is a major glass-forming component. Their scientific importance arises from the combination of a structurally adaptable network and a broad range of composition-dependent physical properties. The chapter reviewed here traces the development of tellurite-glass research from early structural measurements to modern heavy-metal-oxide and rare-earth-doped systems. It also shows how the understanding of local Te–O coordination has gradually become connected with optical and photonic performance.

The classical literature established an important structural point: the glassy state does not necessarily require the complete destruction of the short-range structural units found in the corresponding crystal. Barady's X-ray investigations of TeO₂ glass showed well-defined features in the radial distribution function (RDF), including prominent Te–O correlations, and led to the conclusion that the glass retained important aspects of the coordination found in crystalline TeO₂ [1,2]. This observation became particularly significant because conventional glass-formation criteria were strongly influenced by tetrahedrally coordinated oxide networks.

Later studies expanded the compositional space of tellurite glasses. The use of alkali and heavy-metal oxides, rare-earth oxides and other modifiers permits systematic control of density, refractive index, optical band gap, thermal stability, luminescence and network structure. The chapter therefore presents tellurite glass as a tunable functional material rather than simply as a conventional glass former. Modern work also demonstrates that tellurite compositions can support crystalline inclusions, nanoparticles and glass-ceramic structures when suitable heat-treatment or compositional conditions are applied [6–22].

2. Classical Development and Structural Basis of Tellurite Glasses

2.1 Early X-ray investigations

Barady's 1956 and 1957 investigations are presented in the chapter as the earliest systematic reports on tellurium-oxide glass [1,2]. TeO₂ was fused with a small quantity of Li₂O-containing material, and X-ray measurements were used to study the radial distribution of electrons and the local atomic arrangement. The RDF contained strong peaks near 1.95 and 2.75, with additional features at larger radial distances. The nearest-neighbour distances were

interpreted mainly in terms of Te–O coordination, while the longer-range features were associated with Te–Te distributions [1,2].

An important result was that the area of the principal RDF peaks was consistent with a central Te atom surrounded by approximately four close oxygen neighbours and two additional oxygen atoms at a larger distance. The chapter therefore emphasizes a distorted, approximately octahedral local environment rather than a simple tetrahedral network. The persistence of these short-range structural characteristics after conversion from crystal to glass was considered evidence that glass formation did not require complete reconstruction of the local TeO₂ structural unit [1,2].

2.2 Glass formation and the challenge to classical criteria

Winter's work connected glass formation with the connectivity of vitreous networks and distinguished self-vitrifying elements from components that participate in binary or multicomponent glasses [3]. The chapter places this discussion alongside the geometrical criteria proposed by Zachariasen and the radius-ratio observations associated with Goldschmidt [4]. Conventional criteria emphasized oxygen tetrahedra as favourable structural units for glass formation. TeO₂ is noteworthy because its local coordination is not adequately described by a simple tetrahedral picture.

In TeO₂, the covalent character of Te–O bonding and the distorted octahedral environment allow a degree of structural flexibility. The addition of modifiers such as Li₂O or Na₂O can disrupt selected Te–O connections and provide charge-balancing ions. According to the classical discussion, only a limited amount of modifier is required to promote vitrification, indicating that complete conversion to a corner-sharing tetrahedral network is not necessary [1–4]. This structural flexibility is one reason tellurite glasses can accommodate a broad variety of additional components.

2.3 Structural units and short-range order

The chapter describes crystalline tellurite and paratellurite structures as containing four-coordinated Te environments with strong Te–O bonding. In glass, related TeO₄ units can coexist with lower-coordination environments, and subsequent studies of modified tellurite glasses have identified TeO₃ and TeO₄ structural units. The balance between these units is composition-dependent and can be influenced by rare-earth oxides, silver-containing modifiers and other network components [20,22,37].

This structural picture is particularly useful when interpreting optical and thermal measurements. A change in modifier concentration can alter network connectivity, bond character, free volume and polarizability. These changes can subsequently affect refractive

index, optical band gap, density, molar volume, thermal stability and rare-earth-ion emission. Thus, structural characterization is not merely descriptive; it provides the basis for understanding composition–property relationships in tellurite materials [5,6,20,22].

3. Composition, Modifiers and Heavy-Metal-Oxide Tellurite Glasses

One of the central themes in the chapter is the ability of tellurite glass to accept additional oxides and functional dopants. The database-oriented approach discussed by Yasui and Utsuno highlights the importance of compositional additivity and systematic materials design [5]. In practice, tellurite networks have been modified with ZnO, WO₃, Na₂O, PbO, Sb₂O₃, Bi-containing components and rare-earth oxides. These modifications can be used to tune structural, optical, thermal and radiation-interaction properties.

3.1 ZnO and tungsten-containing systems

Kumbhakar et al. investigated heavy-metal-oxide-doped tellurite glasses with compositions based on TeO₂–WO₃–ZnO and examined the influence of ZnO on physical, structural, thermal and optical characteristics [6]. Differential scanning calorimetry was used for thermal analysis, X-ray diffraction for structural assessment and Raman spectroscopy for structural units. Density, molar volume, polaron radius and intermolecular distance were also evaluated. Optical absorption in the 350–1000 nm range was used to determine refractive index, direct and indirect optical band gaps and Urbach energy [6].

These measurements illustrate a general strategy in tellurite-glass research: composition is varied systematically and the resulting changes are interpreted through complementary structural, thermal and optical measurements. Such an approach is essential because the same modifier can affect several properties simultaneously. A composition that improves optical performance may also alter thermal stability or network connectivity, making multi-property characterization necessary.

3.2 Erbium-containing tellurite glasses

Elkhoshkhany and co-workers studied a quaternary erbium tellurite system with a composition based on TeO₂–ZnO–Na₂O–Er₂O₃ [7]. UV–visible measurements, thermal analysis and structural characterization showed that increasing Er₂O₃ concentration was associated with changes in the optical band gap and thermal behaviour. Nanoscale phases including Zn₂Te₃O₈, TeO₂, ZnO and Er-containing tellurium oxides were identified after thermal treatment [7].

The study is important because it demonstrates the transition from a simple amorphous-glass description to a more complex glass/phase-development picture. Heat treatment can induce

structural modification and crystallization, and these changes may alter optical properties. The chapter reports that annealing was accompanied by a reduction in optical energy gap after structural modification [7].

3.3 Samarium-doped HMO glasses and radiation shielding

AlMisned et al. examined tellurite–tungstate–antimonate heavy-metal-oxide glasses containing Sm_2O_3 and evaluated their photon and fast-neutron attenuation characteristics using MCNPX and Phy-X/PSD approaches [8]. The compositions were varied by replacing part of TeO_2 with Sm_2O_3 . Increasing Sm_2O_3 concentration increased sample density and produced measurable changes in attenuation-related parameters. The study considered linear and mass attenuation coefficients, half-value layer, mean free path, effective atomic number, exposure/build-up factors and fast-neutron removal cross section [8].

The reported results indicate that heavy-metal-oxide tellurite glasses can be designed not only for optical functions but also for radiation-interaction applications. This broadens the technological significance of tellurite materials and demonstrates how compositional engineering can target a property that is not directly related to optical transmission or luminescence.

4. Telluride/Tellurite-Related Lead Systems and Nanostructured Materials

The chapter also reviews materials in which tellurium is combined with lead-containing systems, including lead telluride (PbTe), lead tellurite glasses and glass ceramics. These materials provide a bridge between amorphous glass science and semiconductor or nanocrystal research.

4.1 PbTe-based amorphous alloys and thermoelectric behaviour

Li, Qi and Wang investigated PbTe-based amorphous alloys with emphasis on glass formation and thermoelectric properties [11]. Their analysis indicated that glass-forming ability was governed by thermodynamic and kinetic factors, with low entropy of fusion and a deep eutectic region identified as important factors. A glass-forming region was reported for the $(\text{PbTe})_x(\text{Ga}_2\text{Te}_3)_{100-x}$ system, with an optimum composition exhibiting low thermal conductivity [11].

The ability to reduce lattice thermal conductivity through structural disorder is attractive for thermoelectric materials. In this context, glass formation is not simply a route to an amorphous optical material; it becomes a means of controlling heat transport. The chapter therefore places tellurium-containing glasses at the intersection of glass science, semiconductor materials and energy-related applications.

4.2 Niobium-doped lead telluride glass ceramics

Sathish and co-workers investigated niobium-doped lead-telluride glass ceramics prepared by melt quenching and subsequent heat treatment [12,15]. The as-prepared samples were amorphous, whereas annealing promoted crystalline development. X-ray diffraction and scanning electron microscopy were used to follow crystallization and particle morphology. The reported crystallite dimensions were in the nanometre scale, illustrating the possibility of producing controlled glass-ceramic microstructures through thermal treatment [12,15].

4.3 PbTe quantum dots and thin films

El-Rabaie et al. reported PbTe quantum dots formed in a fluorogermanate glass matrix [13]. Heat treatment produced nanoparticles with different sizes, and the optical absorption exhibited a blue shift associated with quantum confinement. The optical band-gap behaviour changed as the quantum-dot size increased, while X-ray diffraction and transmission electron microscopy supported the presence and size evolution of cubic PbTe nanocrystals [13].

Antimony-doped PbTe thin films were also examined for structural and optical changes [14]. The incorporation of Sb altered lattice parameters and crystallite dimensions and increased the optical band gap within the reported range. These studies show how tellurium-containing materials can be engineered from bulk amorphous glass to nanoscale semiconductor structures with size- and composition-dependent optical responses [13,14].

4.4 Lead-doped tellurite glasses and electrical switching

Riyatun and Marzuki investigated Pb-containing tellurite glasses and found changes in refractive index and optical band-gap parameters with Pb^{2+} concentration [16]. Saheb et al. examined lead-doped germanium telluride glasses and reported threshold-type electrical switching behaviour [17]. The switching voltage decreased with increasing lead concentration over the studied composition range, demonstrating the possibility of electrically active tellurium-containing amorphous materials [17].

4.5 Upconversion and Yb/Er-containing systems

Bomfim et al. studied $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped $\text{PbO-GeO}_2\text{-Ga}_2\text{O}_3$ glasses and examined upconversion under 980 nm excitation [18]. Emission bands in the green and red spectral regions were observed, and increasing Yb^{3+} concentration modified the balance between red and green emission through energy transfer from Yb^{3+} to Er^{3+} . This demonstrates the usefulness of sensitizer/activator combinations for controlling upconversion colour and intensity.

Wang et al. investigated Yb^{3+} -containing lead-zinc-telluride oxide glasses and reported useful fluorescence linewidth, emission cross section and lifetime characteristics [19]. These

properties support the potential of such glasses as gain media for diode-pumped and tunable laser systems [19].

5. Structural Modification by PbO, Ag₂O and Ag Nanoparticles

Structure–property relationships are particularly evident in PbO- and Ag-modified tellurite glasses. Silva et al. used Raman scattering and X-ray absorption spectroscopy to investigate TeO₂–PbO glasses [22]. Increasing PbO changed the coordination environment around tellurium, supporting the interpretation of Pb as a modifier of the glass network. The study also indicated a medium-range-order contribution, suggesting that Pb can influence more than the immediate Te–O coordination.

Al Mohammadi et al. examined PbI₂–Ag₂O–TeO₂ glasses using Raman spectroscopy, X-ray diffraction and electron diffraction techniques [20]. The work identified TeO₄ and TeO₃₊₁ as important structural building units, while increasing PbI₂ promoted TeO₃-related species and Ag–Te species. Ag-containing systems also showed evidence of crystalline clusters or metastable crystalline phases under appropriate conditions [20].

Silver nanoparticles provide another route for modifying rare-earth luminescence. Dousti and Amjad reported enhanced emission in Nd³⁺-doped lead-tellurite glasses containing Ag nanoparticles, with a surface plasmon band near 522 nm and enhanced Nd³⁺ luminescence at suitable Ag concentrations [36]. The proposed interpretation involves local-field enhancement and energy-transfer interactions between metal nanoparticles and rare-earth ions. Similar work on Er³⁺-doped zinc tellurite glass showed that AgCl could improve thermal stability and, at an optimum concentration, strongly enhance luminescence before concentration quenching occurred [9].

6. Rare-Earth-Doped Tellurite Glasses for Laser and Photonic Applications

6.1 Nd³⁺-doped tellurite gain media

Rare-earth doping is one of the most important application-oriented developments in tellurite-glass research. Nd³⁺ is particularly significant because its emission near 1.06 μ m is compatible with important laser and amplifier technologies. Richards and Jha reviewed tellurite-glass gain media and emphasized the relevance of rare-earth-doped tellurite compositions for lasers [23]. Michel et al. reported an early tellurite bulk-glass laser using Nd doping and an excitation wavelength of 514.5 nm, with laser operation near 1060 nm [24].

Wang et al. subsequently demonstrated a Nd-doped tellurite single-mode fibre laser [25]. The chapter describes a tellurite fibre composed of a Nd-containing core and a tellurite cladding

and reports a measured slope efficiency of approximately 23% at one end under the stated pumping conditions [25]. This work established an important link between the favourable spectroscopic properties of tellurite glass and practical fibre-laser architectures.

6.2 Tellurite microsphere lasers

Anashkina reviewed rare-earth-doped tellurite fibres and microspheres as laser sources [26]. Sasagawa et al. demonstrated Nd-doped tellurite microsphere lasing [27] and subsequently showed that a distributed-feedback structure could control the lasing wavelength [28]. These studies introduced microspherical resonators as compact laser platforms in which high optical confinement can be achieved through whispering-gallery modes and related resonant structures.

Later work extended this concept through air-bubble-containing microspheres and localized thermal fabrication. Kishi et al. demonstrated on-chip fabrication of air-bubble-containing Nd³⁺-doped tellurite microspheres [29], while subsequent work explored terrace structures and quasi-single-mode output [30]. Kumagai et al. reported low-threshold lasing using non-whispering-gallery-mode excitation in bubble-containing microspheres [31]. Together, these studies illustrate how geometric modification of a tellurite microresonator can alter mode selection and threshold behaviour.

6.3 Nd³⁺ optical properties and silver enhancement

Azman et al. evaluated the lasing efficiency of Nd³⁺-doped lead tellurite glass and discussed the optical properties of Nd³⁺ in the context of laser emission around 1.06 μm [32]. Bolundut et al. investigated Nd³⁺-doped lead tellurite glass ceramics containing silver and found that Nd concentration influenced structural, spectroscopic and magnetic behaviour [33]. Photoluminescence quenching was observed above a concentration threshold, illustrating the need to balance activator concentration against concentration-induced interactions.

Azlina et al. investigated tellurite glasses containing neodymium nanoparticles and evaluated their density, molar volume, nonlinear optical response, photoluminescence and UV–visible behaviour [34]. The reported optical band-gap range was approximately 3.178–3.209 eV, and excitation around 800 nm produced upconversion emission. These results reinforce the potential of Nd-containing tellurite glasses for nonlinear and laser-phonic applications.

Shigihalli et al. examined Nd³⁺-doped lead-tellurite-borate glasses using absorption spectroscopy and Judd–Ofelt analysis [35]. Radiative transition parameters, branching ratios and related quantities were evaluated, and the reported emission characteristics suggested potential for laser applications. Dousti and Amjad further showed that Ag nanoparticles can enhance the 1.06 μm emission of Nd³⁺-doped lead-tellurite glass [36].

7. Er³⁺, Yb³⁺ and Other Rare-Earth Systems

Er³⁺- and Yb³⁺-containing tellurite glasses provide complementary emission pathways, particularly for upconversion and infrared photonics. The Yb³⁺/Er³⁺ system can exploit efficient energy transfer from Yb³⁺ sensitizers to Er³⁺ activators, as demonstrated in PbO–GeO₂–Ga₂O₃ glasses [18]. In Er³⁺-doped zinc tellurite glasses, AgCl addition altered thermal stability and spectroscopic behaviour [9].

Culea et al. examined Er³⁺-doped lead tellurite glass ceramics with Ag₂O or metallic Ag nanoparticles [37]. XRD, FTIR, XPS and photoluminescence measurements showed that the network contained TeO₃ and TeO₄ structural units. The conversion between these units depended on Er₂O₃ concentration and the silver codopant. The optical band gap decreased with increasing erbium content, and the emission response of Er³⁺ was modified by Ag codoping [37].

These results demonstrate that rare-earth concentration and nanoparticle incorporation should be considered together. The optical response cannot always be predicted from the rare-earth concentration alone because local structure, clustering, modifier chemistry and plasmonic interactions can all contribute to the observed emission.

8. Processing and Characterization Approaches

The studies reviewed in the chapter employ a recurring set of preparation and characterization methods. Melt quenching is widely used to obtain homogeneous amorphous glasses, while controlled annealing is used to promote nucleation and crystallization when glass ceramics or nanocrystalline phases are desired. Differential scanning calorimetry is important for identifying glass-transition and crystallization behaviour, whereas X-ray diffraction distinguishes amorphous glasses from crystalline or partially crystallized materials [6,7,12,15].

Raman and FTIR spectroscopies provide information on Te–O vibrational units and are especially useful for identifying changes in TeO₃/TeO₄ populations [6,20,37]. UV–visible and near-infrared spectroscopy provide absorption edges, optical band gaps and rare-earth transitions, while photoluminescence measurements reveal emission wavelengths, intensity and concentration quenching [7,9,18,33–37]. Electron microscopy and related diffraction methods are important when nanoparticles, quantum dots or microstructural phases are present [13,20].

For radiation-shielding applications, calculated attenuation parameters and Monte Carlo methods complement experimental characterization [8,10]. For laser materials, spectroscopic

parameters such as oscillator strengths, radiative lifetimes, emission cross sections and Judd–Ofelt intensity parameters help determine whether a composition is suitable as a gain medium [23–26,35]. The overall literature therefore supports a multi-technique approach in which structural, thermal, optical and application-specific measurements are interpreted together.

9. Applications and Future Research Directions

The literature assembled in the chapter indicates that tellurite glasses have a broad application space. Their high refractive index, compositional flexibility and rare-earth compatibility support optical fibres, waveguides, lasers, microspherical resonators and nonlinear optical devices [23–37]. Heavy-metal-oxide compositions can also be engineered for radiation attenuation [8,10]. PbTe-related systems add potential in thermoelectric, semiconductor and quantum-dot technologies [11–14].

Several research directions emerge from the reviewed studies. First, a more quantitative connection between TeO₃/TeO₄ populations, modifier concentration and macroscopic properties would strengthen composition design. Second, controlling crystallization at the nanoscale may allow glasses and glass ceramics to combine the processing advantages of an amorphous host with the functional properties of nanocrystals [7,12–15]. Third, rare-earth/metal-nanoparticle codoping offers a route to tune local optical fields and emission, but concentration quenching and reproducibility remain important design considerations [9,33,36,37].

Future work should also emphasize processing–structure–property relationships rather than treating composition and performance as independent variables. For laser glasses, this means linking network structure and rare-earth site symmetry to emission cross section and lifetime. For shielding glasses, it means balancing density and attenuation with mechanical and thermal stability. For nanostructured systems, it requires precise control of particle size, distribution and crystallization kinetics. The database-oriented strategy discussed by Yasui and Utsuno provides a useful conceptual framework for such systematic materials development [5].

10. CONCLUSION

Tellurite glasses have evolved from a structurally unusual class of oxide glasses into a versatile family of functional materials. The classical studies of Barady demonstrated that the local coordination of TeO₂ can persist in the glassy state and provided an early structural basis for understanding tellurite vitrification [1,2]. Winter's glass-formation work and the

broader framework associated with Goldschmidt helped place these observations within the developing science of glass structure [3,4].

Modern research has expanded tellurite glasses through ZnO, WO₃, PbO, Sb₂O₃, rare-earth oxides, halide components and metallic nanoparticles. These compositional changes enable control over thermal stability, optical band gap, refractive index, luminescence, radiation attenuation and crystallization behaviour [6–22]. The most technologically mature direction is rare-earth-doped tellurite photonics, where Nd³⁺-doped fibres and microspheres have demonstrated laser operation and where Ag nanoparticles can further modify emission [23–37].

Overall, the chapter-supported literature shows that the major strength of tellurite glass is its structural and compositional adaptability. Continued progress will depend on establishing clearer quantitative links between local structure, processing conditions and functional performance. Such understanding can accelerate the design of next-generation tellurite glasses for lasers, optical amplification, nonlinear photonics, radiation shielding, thermoelectrics and nanostructured devices.

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