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JAQUELINE VALESKI GUNHA

**TEO₂-ZNO GLASSES INCORPORATING LI₂O, NA₂O, TIO₂, MOO₂, AND BAO
FOR OPTIMIZATION IN RADIATION SHIELDING**

**VIDROS DE TeO₂-ZnO INCORPORANDO Li₂O, Na₂O, TiO₂, MoO₂ e BaO
PARA OTIMIZAÇÃO NA BLINDAGEM DE RADIAÇÃO**

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Dissertation presented to the Graduate Program in Sciences, concentration area Physics, at the Universidade Estadual de Ponta Grossa, in partial fulfillment of the requirements for the degree of Doctor in Science.

Advisor: Prof. Dr. Andressa Novatski

Co-advisor: Prof. Dr. Robson Ferrari Muniz

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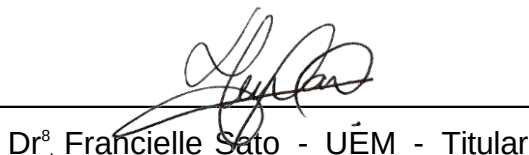
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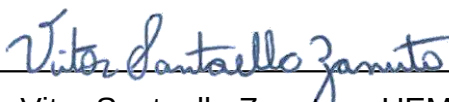


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The marathon I didn't run and the equation I didn't solve.

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"What does not kill me makes me stronger."

Friedrich Nietzsche

ABSTRACT

This dissertation focuses on the development and characterization of tellurite glasses with enhanced radiation shielding capabilities, with the aim of providing efficient materials for protection against ionizing radiation. The glasses were studied in a ternary system to optimize their structural, thermal, optical, and shielding properties. XRD confirmed the amorphous nature of the samples, while scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) demonstrated homogeneous surfaces and a uniform chemical composition. Raman and FTIR spectroscopic analyzes identified key structural units, highlighting the influence of modifiers such as TiO_2 and MoO_3 . These oxides were shown to increase non-bridging oxygen (NBO) concentrations, improve structural arrangement, and enhance radiation absorption. The density and oxygen packing density (OPD) analyzes revealed significant changes with the introduction of modifiers. BaO notably increased density and improved structural stability, while Na_2O reduced compactness, resulting in a less cohesive network. Differential scanning calorimetry (DSC) indicated that TiO_2 and BaO enhanced thermal stability, increasing the glass transition temperature (T_g) and the crystallization onset temperature (T_x). In contrast, Na_2O showed lower thermal stability. UV-Vis spectroscopy confirmed the glasses high efficiency in absorbing UV and visible radiation. The calculated optical band gap (2.18–3.74 eV) and Urbach energy provided information on the electronic structure, revealing the role of modifiers in the tuning of optical properties. Mechanical characterization through Vickers hardness tests demonstrated superior mechanical strength in glasses modified with TiO_2 and reduced hardness with Na_2O , correlating with the observed structural compactness. Optical microscopy corroborated the homogeneity of the materials, confirming the absence of structural defects. Radiation shielding studies showed that the incorporation of BaO and MoO_3 significantly improved gamma and neutron attenuation. BaO increased density and cross-linking, optimizing gamma radiation absorption, particularly at lower photon energies. MoO_3 improved fast neutron shielding due to its higher density and structural rearrangement induced by molybdenum oxides. The mass attenuation coefficients (MAC) demonstrated that the tellurite glasses surpassed conventional shielding materials, such as lead and barite concrete, particularly at low photon energies. Half-value layer (HVL) measurements further underscored their effectiveness, achieving substantial protection with thinner layers, advantageous for lightweight and transparent shielding applications. These findings highlight the versatility of tellurite glasses as advanced materials for radiological environments, offering a combination of transparency, mechanical robustness, and superior radiation attenuation for various technological and industrial applications.

Key-words: Tellurite Glasses, Radiation Shielding, Optical Properties, Mass Attenuation Coefficient, Structural analysis.

RESUMO

Esta tese concentra-se no desenvolvimento e caracterização de vidros de telureto com capacidades aprimoradas de blindagem contra radiação, visando fornecer materiais eficientes para proteção contra radiação ionizante. Os vidros foram estudados em um sistema ternário para otimizar suas propriedades estruturais, térmicas, ópticas e de blindagem. A DRX confirmou a natureza amorfa das amostras, enquanto a MEV e a EDS demonstraram superfícies homogêneas e composição química uniforme. As análises espectroscópicas Raman e FTIR identificaram unidades estruturais-chave, destacando a influência de modificadores como TiO_2 e MoO_3 . Esses óxidos demonstraram aumentar as concentrações de NBO, melhorar o arranjo estrutural e aprimorar a absorção de radiação. As análises de densidade e OPD revelaram mudanças significativas com a introdução de modificadores. O BaO aumentou notavelmente a densidade e melhorou a estabilidade estrutural, enquanto o Na_2O reduziu a compactação, resultando em uma rede menos coesa. A DSC indicou que TiO_2 e BaO aumentaram a estabilidade térmica, elevando a T_g e a T_x . Em contraste, o Na_2O apresentou menor estabilidade térmica. A espectroscopia UV-Vis confirmou a alta eficiência dos vidros na absorção de radiação UV e visível. O intervalo calculado para a largura da banda proibida óptica (2,18–3,74 eV) e a energia de Urbach forneceram informações sobre a estrutura eletrônica, revelando o papel dos modificadores na modulação das propriedades ópticas. A caracterização mecânica, por meio de testes de dureza Vickers, demonstrou maior resistência mecânica em vidros modificados com TiO_2 e menor dureza com Na_2O , correlacionando-se com a compactação estrutural observada. A microscopia óptica corroborou a homogeneidade dos materiais, confirmando a ausência de defeitos estruturais. Estudos de blindagem contra radiação mostraram que a incorporação de BaO e MoO_3 melhorou significativamente a atenuação de raios gama e nêutrons. O BaO aumentou a densidade e a conectividade estrutural, otimizando a absorção de radiação gama, particularmente em baixas energias de fótons. O MoO_3 aprimorou a blindagem contra nêutrons rápidos devido à sua maior densidade e ao rearranjo estrutural induzido pelos óxidos de molibdênio. Os MAC demonstraram que os vidros de telureto superaram materiais de blindagem convencionais, como chumbo e concreto baritado, especialmente em baixas energias de fótons. As medições da HVL reforçaram ainda mais sua eficácia, alcançando proteção substancial com camadas mais finas, o que é vantajoso para aplicações de blindagem leves e transparentes. Esses resultados destacam a versatilidade dos vidros de telureto como materiais avançados para ambientes radiológicos, oferecendo uma combinação de transparência, robustez mecânica e superior atenuação de radiação para diversas aplicações tecnológicas e industriais.

Palavras-chave: Vidros de Telureto, Blindagem contra Radiação, Propriedades Ópticas, Coeficiente de Atenuação de Massa, Caracterização Estrutural.

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1 INTRODUCTION

In recent years, the search for efficient radiation shielding materials has gained significant momentum as a result of their critical role in the addressing global challenges. This interest aligns with key Sustainable Development Goals (SDGs) established by the United Nations, particularly SDG 3 (Good Health and Well-being), SDG 9 (Industry, Innovation, and Infrastructure), SDG 11 (Sustainable Cities and Communities), and SDG 13 (Climate Action). These goals emphasize the need for innovative and cost-effective solutions to mitigate the risks associated with ionizing radiation in various applications (Nations, 2015).

The development of new radiation shielding materials is increasingly driven by the need to align with Sustainable Development Goals (SDGs), prioritizing safety enhancements and reduced environmental impact. Conventional shielding materials, particularly lead-containing glasses, pose significant health and environmental risks due to lead toxicity. This has created an urgent demand for lead-free alternatives capable of delivering comparable or superior shielding performance. Among these alternatives, tellurite glasses stand out due to their unique properties, including high density (Sidek et al., 2009), excellent infrared transmittance (Kabalcı et al., 2011), robust resistance to radiation-induced damage (Meyers; Chawla, 2008), and the flexibility to incorporate various modifiers to optimize their protective properties (Sayyed et al., 2023a). These characteristics position tellurite glasses as a transformative solution in radiation shielding, offering enhanced safety in industrial and medical applications while adhering to sustainability goals. Their development exemplifies a significant technological advance that not only raises safety standards, but also supports the transition toward environmentally sustainable innovation (El-Mallawany, 2016; Zaki et al., 2018; Gunha et al., 2024b).

Tellurite glasses exhibit remarkable chemical complexity and a high atomic number, which impart an exceptional capacity to absorb ionizing radiation. This effectiveness is quantitatively represented by the linear attenuation coefficient, a key parameter that measures the fraction of radiation absorbed per unit thickness of material. Materials with higher linear attenuation coefficients, such as tellurite glasses, demonstrate superior radiation absorption capabilities, making them ideal candidates for shielding applications (Çağlar et al., 2021; Hanfi et al., 2021; Alonizan et al., 2023).

The inherent density of pure tellurite glass (≈ 5.6 to 6.1 g/cm³) further enhances its shielding properties, as it significantly surpasses that of common glass types, including soda-lime (≈ 2.4 to 2.5 g/cm³), borosilicate (≈ 2.2 to 2.4 g/cm³), silica glass (≈ 2.2 g/cm³), and aluminosilicate (≈ 2.5 to 2.7 g/cm³) (El-Mallawany, 2016). This direct correlation between density and shielding efficacy underscores the advantages of tellurite glasses in radiation protection. In addition, their unique optical properties, including infrared, visible, and ultraviolet radiation transparency, allow their use in specialized ap-

plications, such as protective windows and visors, without compromising visibility. This dual functionality is particularly advantageous in medical and research settings, where clear observation is critical for safety and operational efficiency (Clermont-Gallerande et al., 2020; Rammah et al., 2020a; Rammah et al., 2020b; Wu et al., 2023; Zhao et al., 2024).

In summary, radiation shielding is essential to protect both humans and equipment from ionizing radiation. Tellurite glasses are highly effective in this role, because of their ability to block ionizing radiation and their optical transparency to nonionizing radiation. Their shielding efficiency, determined by linear attenuation coefficients and high density, makes them ideal materials for environments where radiation is routinely used for medical, industrial, and research purposes.

The main objective of this dissertation is to develop and characterize tellurite glasses for applications in radiation shielding.

- To prepare and evaluate the glass-forming ability and feasibility of new tellurite glass matrices for potential applications in radiation shielding and optical devices;
- To characterize the physical and structural properties of new tellurite glass matrices with varying network modifiers in the $\text{TeO}_2\text{-ZnO}$ matrix;
- To study the optical properties of tellurite glasses with different network modifiers;
- To evaluate the effectiveness of tellurite glasses as radiation shielding materials;
- To investigate the correlation between glass composition, mechanical properties, and their capacity for radiation protection.

Thus, this dissertation is organized into four chapters and three appendices, in addition to this introduction, as follows:

Chapter 2: Theoretical Framework This chapter provides an overview of glass, including its history, definitions, and vitrification criteria. The chapter discusses structural and kinetic theories relevant to glass formation and highlights the applications of tellurite glasses. The key concepts of radiation shielding and its theoretical models are introduced, along with a comparative analysis of tellurite glasses with other types of glasses.

Chapter 3: Materials and Methods This chapter describes the experimental procedures employed to synthesize and characterize the tellurite glass samples. Structural properties were investigated using XRD, Raman spectroscopy, and Fourier transform infrared spectroscopy (FTIR). Physical properties were analyzed through density, molar volume, and oxygen packing density (OPD). Thermal properties were studied using differential scanning calorimetry (DSC). UV-Vis spectroscopy was utilized to determine the optical absorption coefficient, band gap energy, Urbach tail, and oxide-ion polarizability.

Mechanical resistance was assessed through Vickers hardness testing, while optical microscopy enabled crack evolution and microstructural analysis. Detailed microstructural analysis was conducted via scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The radiation shielding properties of the glasses were evaluated using the linear attenuation coefficient (LAC), the mass attenuation coefficient (MAC) and theoretical-experimental comparisons for specific radioisotopes (Co-57 and Am-241). Shield thickness calculations were also performed.

Chapter 4: Results and Discussions This chapter presents the results of the newly developed $\text{TeO}_2\text{-ZnO-X}$ glass compositions, where $\text{X} = \text{Na}_2\text{O}, \text{Li}_2\text{O}, \text{TiO}_2, \text{MoO}_3,$ and BaO , with a focus on improving fast neutron absorption. These compositions address the challenges identified in the simulations discussed in the Appendix C. The findings cover structural, thermal, optical, and radiation properties, highlighting the impact of different modifiers and intermediates on performance.

Chapter 5: Conclusions This chapter summarizes the key findings of the study and highlights the potential of tellurite glasses for radiation shielding and other advanced applications. It also outlines recommendations for future research to further optimize the properties of the material.

Appendix B: Radiation Overview Provides a historical perspective on radiation, an overview of radiation-matter interactions, and the principles of radiation shielding, offering additional context for the main study.

Appendix C: Impact of Glass Composition on Radiation Shielding Effectiveness Presents simulation results for $\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$ and $\text{TeO}_2\text{-Li}_2\text{O-BaO}$ -based compositions. These simulations reveal that, while BaO -modified glasses excel at gamma radiation shielding, they are less effective for fast neutrons. In contrast, MoO_3 -modified glasses, although generally effective, require further optimization for enhanced fast neutron absorption.

Appendix D: Supplemental figures Includes additional figures and graphical data that support the analysis presented in the main chapters.

Appendix E: Academic background Provides an overview of the academic and professional context of this research.

2 THEORETICAL FRAMEWORK

2.1 GLASSES

Glasses are amorphous materials characterized by the absence of a long-range crystalline structure. This structural irregularity grants them unique optical properties, including wide spectral ranges, low optical attenuation, and high material quality, making them indispensable in applications such as optical fibers, waveguides, and electronic devices (Manning et al., 2012; Rojo et al., 1990; Ghribi et al., 2015).

The development of advanced materials increasingly emphasizes high-performance and cost-effective solutions, particularly for radiation shielding. Glasses have gained significant attention due to their compositional versatility and the ability to incorporate various additives. Among these, tellurite glasses have emerged as exceptional materials for radiation shielding, because of their high density and compositional flexibility. Unlike conventional silicate glasses, tellurite glasses integrate heavy metal oxides, significantly enhancing their capacity to attenuate ionizing radiation (Alawaideh et al., 2024; Intachai et al., 2022; Sayyed et al., 2024; Wu et al., 2023).

Recent research has focused on optimizing the optical, thermal, structural, and radiation shielding properties of glasses by incorporating modifiers such as rare-earth ions. This strategy not only improves the performance of tellurite glasses, but also expands their applicability to fields including medical imaging, nuclear safety, and radiation therapy. Compared with other glass families, tellurite glasses possess unique advantages, such as higher refractive indices, lower phonon energies, and superior optical transparency. These characteristics make them ideal for advanced radiation shielding applications (Wu et al., 2023; Sayyed et al., 2024; Sayyed et al., 2023a; Dwaikat et al., 2021). Furthermore, their capacity to incorporate high-atomic-number elements, such as lead, barium, and tungsten, allows for superior attenuation of gamma and X-rays. This positions tellurite glasses as a promising solution for next-generation shielding technologies (Kilic et al., 2021; Jat et al., 2021; Çağlar et al., 2021).

Moreover, tellurite glasses (Patra; Annapurna, 2022; Mahalakshmi et al., 2022) and germanate glasses (Cai et al., 2015) have emerged as leading candidates for various technological applications due to their exceptional properties, including wide infrared transmission, thermal stability (approximately 100°C), chemical durability, low phonon energy (550 cm^{-1}), high refractive index (approximately 1.9 to 2.2), and efficient radiation shielding. For further details on the term "glass" and the vitrification process, refer to Appendix A.

2.2 PROPERTIES OF TELLURIUM OXIDE AS NETWORK FORMER

The potential of tellurium oxide (TeO_2) as a glass formation network was first identified by Berzelius in 1834 (BERZELIUS, 1834), who reported the formation of binary tellurium glasses by adding various metal oxides such as V_2O_5 , WO_3 , and BaO . Later, in 1913, Lenher et al. (Lenher; Wolesensky, 1913) documented the vitrification of Na_2O - TeO_2 and K_2O - TeO_2 systems. By 1952, Stanworth (Stanworth, 1952) further advanced the study of tellurite glasses, sparking continued research into their properties and applications.

Since then, extensive studies have explored TeO_2 as a former network, examining its thermal, structural, optical, electrical, and mechanical properties (Nasu et al., 1990). Research has also highlighted the potential of tellurite glasses in generating third harmonics (Tanabe et al., 1990), doping with rare earth ions for photonics applications, and fabricating glass-ceramics for optical devices (Komatsu et al., 1991). Current efforts focus on applications such as structural and thermal characterization, luminescence studies, and optical property optimization (Gunha et al., 2024b; Clermont-Gallerande et al., 2020).

Tellurite glasses are distinguished by their exceptional properties, including high linear refractive indices (1.9-2.3) and non-linear refractive indices (10^{-13} to 10^{-12} esu), which make them suitable for non-linear optical applications (Dimitrov; Sakka, 1996; Elkhoshkhany et al., 2017). Their relatively low melting points (750–850 ° C) simplify the processing compared to other glass families. With a dielectric constant of 20–30—significantly higher than that of silicate glasses (approximately 7)—tellurite glasses are advantageous for electronic applications (El-Mallawany, 2016). Furthermore, they offer wide infrared transmission windows (3–6 μm) and high transparency (up to 90% in the visible region), coupled with excellent chemical durability. Their low glass transition temperature (260–330°C) facilitates the production of optical fibers and other advanced devices without requiring a controlled atmosphere (Dimitrov; Sakka, 1996; Sidkey et al., 1997; Sabadel et al., 1997; Zaki et al., 2018; Elkhoshkhany et al., 2017).

For radiation shielding, tellurite glasses are particularly promising due to their high density (5.7 g/cm³), enabling efficient absorption of gamma rays and X-rays (Alqahtani et al., 2022). Their compositional flexibility allows the incorporation of modifying oxides, such as BaO , MoO_3 , ZnO , and PbO , to enhance specific physical and shielding properties. This flexibility, combined with their broad optical transparency from visible to infrared wavelengths, makes tellurite glasses suitable for radiation-protected viewing windows (Pu et al., 2023). Furthermore, dopants such as MoO_3 and B_2O_3 improve neutron absorption, a critical property for nuclear environments (Almuqrin et al., 2023; Vedavyas et al., 2024).

Tellurite glasses also exhibit high mass attenuation coefficients, often exceeding traditional materials such as lead and concrete. Their ability to provide effective shielding without sacrificing transparency makes them ideal candidates for radiology laboratories, diagnostic imaging devices, nuclear reactors, and radioactive waste storage facilities. In

addition, their lightweight nature compared to lead makes them advantageous for portable radiology equipment and personal protective gear (Vedavyas et al., 2024; Nazrin et al., 2024; D’Souza et al., 2023).

In summary, the unique combination of high density, compositional flexibility, and superior optical properties makes tellurite glasses a viable and innovative alternative for radiation shielding applications. These materials offer effective protection against gamma rays, X-rays, and neutrons, particularly in scenarios where lightweight and transparent solutions are essential.

2.2.1 Structure of Tellurite Glasses

Glassy TeO_2 is composed of TeO_4 units arranged in a trigonal bipyramidal (tbp) structure. The structure of tellurite glasses derives from units analogous to those found in the crystalline polymorphs of TeO_2 : $\alpha\text{-TeO}_2$ (paratellurite) and $\beta\text{-TeO}_2$ (tellurite). In $\alpha\text{-TeO}_2$, the TeO_4 units are connected by sharing the vertex, while in $\beta\text{-TeO}_2$, they are linked by sharing the edges (El-Mallawany, 2016; Zachariasen, 1932; Zarzycki, 1991; Giehl, 2011; Himei et al., 1994; Neov et al., 1979; Novatski et al., 2019; Zaki et al., 2018).

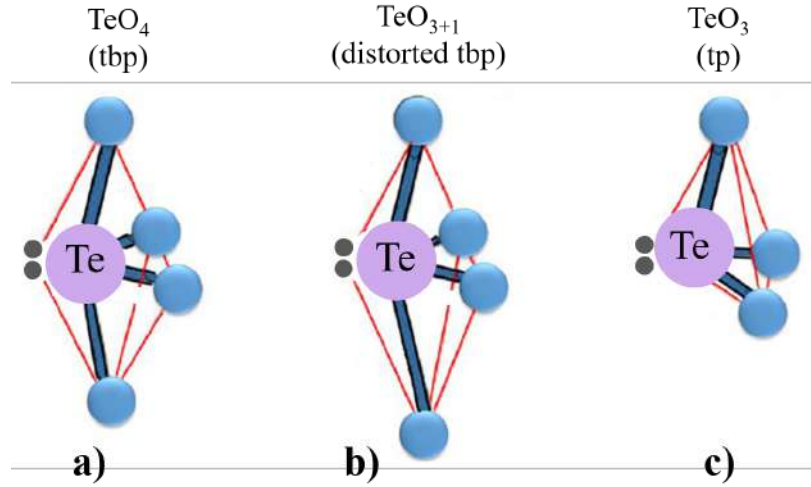
Since tellurium oxide forms glass only under extreme conditions, such as high cooling rates ($> 2 \times 10^2$, K/s) (Bürger et al., 1992), the addition of modifier and intermediate oxides is essential to facilitate the vitrification process. Modifier oxides disrupt the TeO_4 network, altering its structure. For example, alkali oxides transform TeO_4 tbp units into TeO_{3+1} polyhedra and, with further modification, into trigonal pyramidal (tp) TeO_3 units (Berthereau et al., 1996; Chowdari et al., 1998).

In tellurite glasses, three structural configurations of TeO_n units can coexist: TeO_4 , TeO_{3+1} and TeO_3 , as shown in Figure 1 (Stanworth, 1952). In the TeO_4 coordination (Figure 1-a), the tellurium atom occupies the center of a trigonal bipyramid, with two axial oxygen atoms and two equatorial oxygen atoms, while a lone pair of electrons occupies the third equatorial position (Arnaudov et al., 1982). The distances of Te-O bonds differ between axial and equatorial bonds: axial bonds measure approximately 2.08 Å, while equatorial bonds are shorter, around 1.90 Å. The lone electron pair resides in the plane formed by the equatorial oxygens, influencing the geometry and properties of the material.

The structural details, including bond lengths and angles, are fundamental for understanding the physical and chemical behavior of tellurite glasses. Table 1 provides a comprehensive overview of these atomic interactions, providing insight into how the structural configuration impacts the properties of the materials.

Tellurite glass consists mainly of TeO_4 structural units arranged in trigonal bipyramids, where one of the equatorial sites is occupied by a lone pair of non-bonding electrons. Research suggests that the majority of tellurium atoms are interconnected at the vertices

Figure 1 – Structures of tellurium oxide in glasses. (a) TeO_4 trigonal bipyramid, (b) TeO_{3+1} , (c) TeO_3 trigonal pyramid.



Source: adapted (Bürger et al., 1992).

Table 1 – Distances between components in the $\alpha\text{-TeO}_2$ structure.

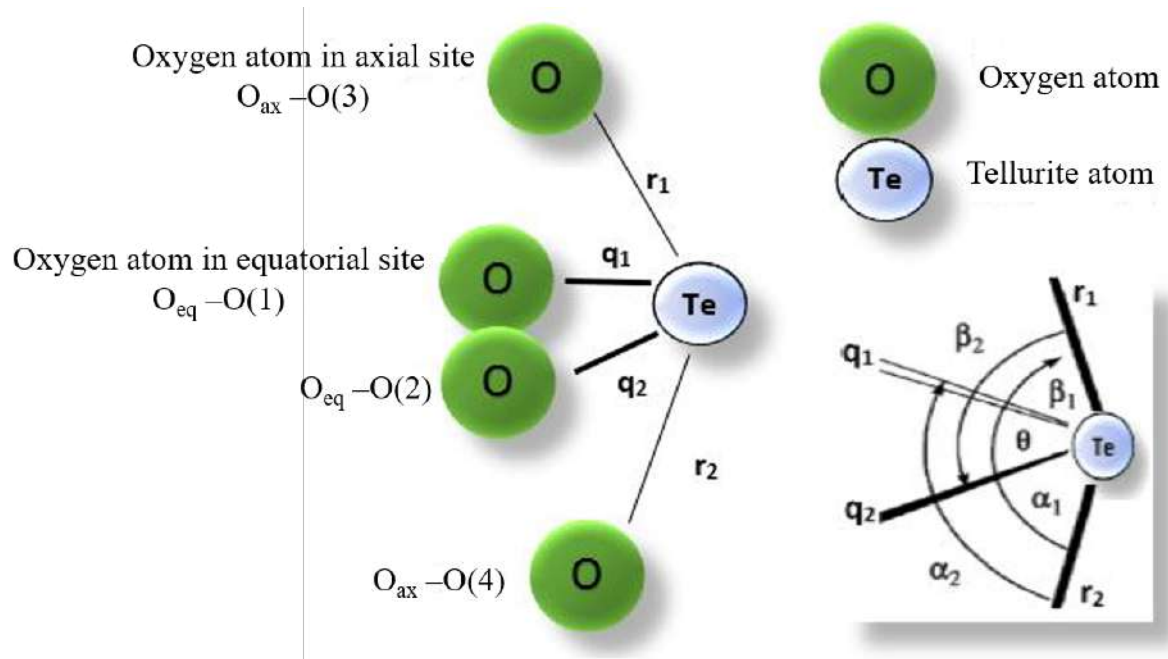
Components	Bond lengths (Å)
Te - O1 = Te - O2	1.903
Te - O3 = Te - O4	2.082
Te - Te	3.740; 3.827; 4.070
O1 - O2	2.959
O1 - O3 = O2 - O4	2.686
O1 - O4 = O2 - O3	2.775
O3 - O4	4.144
Bond angles (°)	
O1 - Te - O2	102.0
O3 - Te - O4	168.5
O1 - Te - O3 = O2 - Te - O4	84.6
O1 - Te - O4 = O2 - Te - O3	88.1
Te - O - Te	139.5

Source: adapted (Neov et al., 1979).

via $\text{Te}-eq\text{O}_{ax}-\text{Te}$ bonds, as depicted in Figure 2 (Sekiya et al., 1992). This structural arrangement significantly influences the physical and optical properties of tellurite glasses, particularly their ability to adapt to various modifications and enhance desired functionalities.

Sekiya et al. proposed that the structural modifications in tellurite glasses are governed by three primary assumptions, as illustrated in the diagram in Figure 3 (Sekiya et al., 1992). These assumptions provide a foundational framework for understanding how changes in the glass composition influence the structural arrangement of TeO_4 , TeO_{3+1} , and TeO_3 units, as well as their impact on the physical and optical properties of the

Figure 2 – Schematic representation of the TeO_4 unit in $\alpha\text{-TeO}_2$ structure.

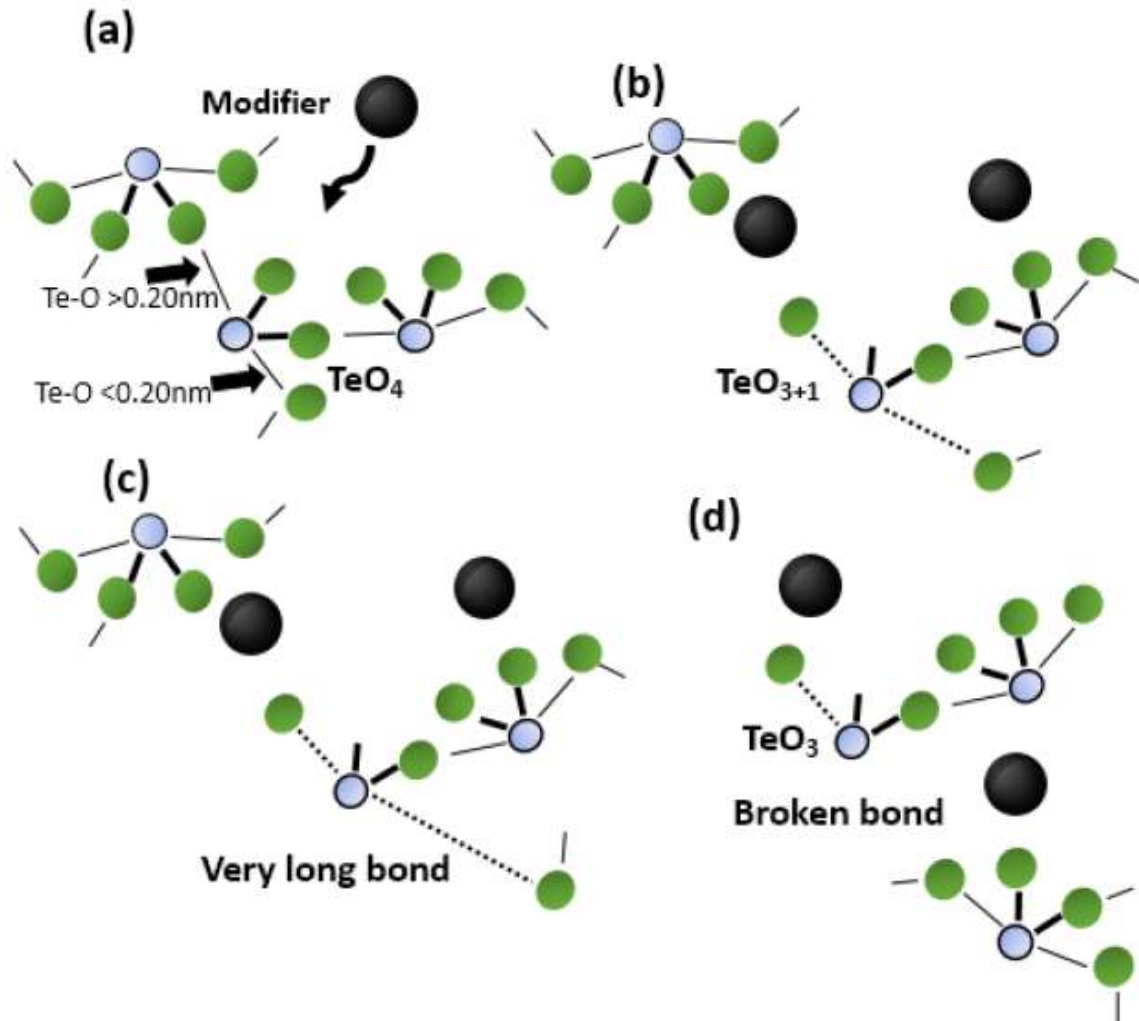


Source: adapted (Strömberg et al., 1985).

material.

- In glasses with a high concentration of tellurium, $\text{Te}-\text{O}-\text{Te}$ linkages occur in two distinct bond types: a short $\text{Te}-\text{O}$ bond (< 0.20 nm) and a long $\text{Te}-\text{O}$ bond (> 0.20 nm), as illustrated in Figure 3 (a). In this configuration, non-bonding oxygens (NBOs) form at the shortest $\text{Te}-\text{O}$ bonds, contributing to structural modifications (Sekiya et al., 1992).
- Structural changes in the coordination state of tellurium, which changes from TeO_4 (tbp) to TeO_{3+1} and eventually to TeO_3 , are driven by the electron-donating capacity of NBO. The introduction of small amounts of alkali oxides breaks $\text{Te}-_{\text{eq}}\text{O}_{\text{ax}}-\text{Te}$ linkages, leading to the formation of NBOs such as $\text{Te}-_{\text{eq}}\text{O}-$ and $\text{Te}-_{\text{ax}}\text{O}-$ in TeO_4 (tbp). These $\text{Te}-_{\text{ax}}\text{O}-$ bonds are unstable, as shown in Figure 3 (b). When the $\text{Te}-_{\text{ax}}\text{O}-$ bond shortens, the opposite $\text{Te}-_{\text{eq}}\text{O}$ bond elongates, transforming the TeO_4 (tbp) unit into a TeO_{3+1} polyhedron, as depicted in Figure 3 (c) (Sekiya et al., 1992).
- The introduction of a second oxide component further modifies the network, elongating and cleaving $\text{Te}-\text{O}$ bonds within TeO_{3+1} units due to electron transfer and the influence of modifier ions, promoting structural transformation (Sekiya et al., 1992).

Figure 3 – Detailed mechanism of structural changes in tellurite glasses - influencing factors and modifications



Source: adapted (Sekiya et al., 1992).

As a result, TeO_3 (tp) units with $\text{Te}-\text{O}-$ and $\text{Te}=\text{O}$ bonds are formed, complete the structural evolution, as illustrated in Figure 3 (d).

2.3 RADIATION SHIELDING

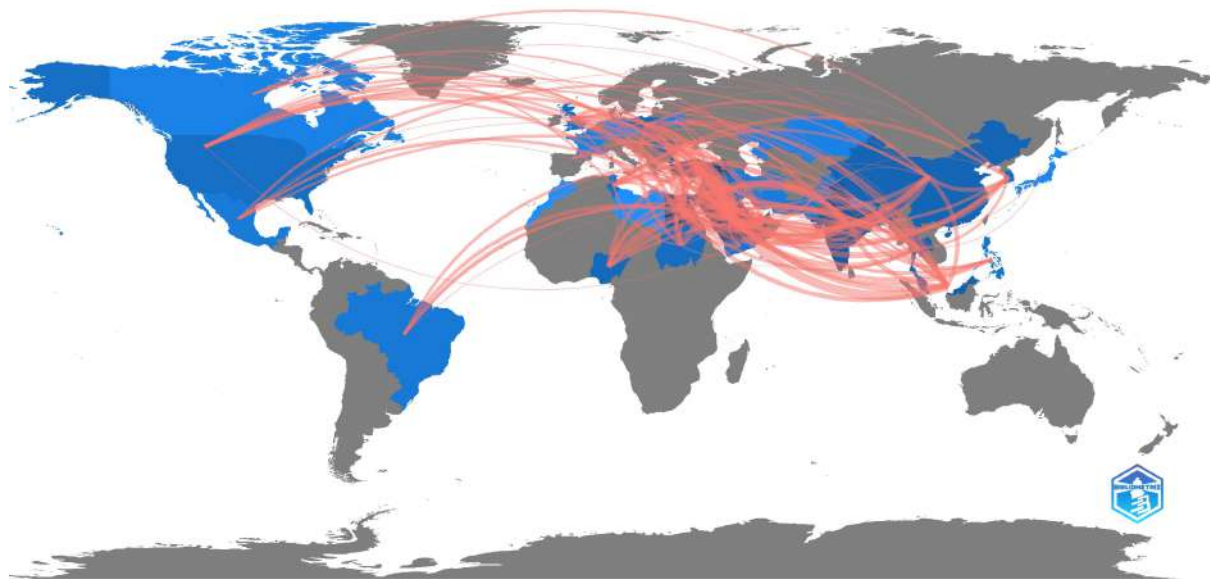
To gain a comprehensive understanding of the research landscape on the development of glasses for radiation shielding applications, a bibliometric analysis was performed using the Scopus database, supported by R software and the Bibliometrix package (Derviş, 2019). The initial search, employing the term 'radiation AND shielding' over the period from 1922 to 2024, identified 28.597 relevant publications. This dataset reflects the extensive global research efforts dedicated to exploring materials for radiation protection across various applications.

Focusing on the unique properties of glasses, such as their capability to absorb

gamma radiation and neutrons—attributes that make them particularly advantageous for radiological protection—the search was refined by including the term “glass”. This narrowed the results to 2,582 articles published between 1935 and 2024, underscoring the increasing recognition of glasses as viable materials for radiation shielding. The literature reveals a growing interest in understanding the relationships between the structural, thermal, and chemical characteristics of glasses and their radiation absorption capabilities. This trend reflects a concerted effort to develop compositions that optimize shielding efficiency, enabling advancements in both industrial and medical applications.

Figure 4, generated using the Bibliometrix package, depicts the Countries Collaboration World Map, highlighting the geographical distribution of research efforts and international partnerships in the development of radiation shielding glasses. The map reveals a robust network of scientific and technological collaborations with significant contributions from Europe, North America, and Asia. Countries such as the United States, China, and Germany emerge as key players, distinguished by their high volume of publications and active international collaborations. This leadership underscores their pivotal role in advancing radiation protection technologies and fostering global progress in the field.

Figure 4 – World collaboration map of countries involved in research on radiation shielding glasses, generated using Bibliometrix. The most active countries are highlighted in blue, while red lines represent international scientific collaborations. This map illustrates the global network of efforts dedicated to developing materials for radiological protection, based on data analyzed in April 2024.



These international collaborations are pivotal in advancing materials science for radiological protection, facilitating the exchange of critical knowledge and technological innovations essential for developing glasses with superior shielding properties. The field of shielding glass research is constantly evolving, driven by the need to design compositions that effectively absorb gamma and neutron radiation, thereby reducing exposure to ionizing particles. This progress not only improves safety standards, but also addresses

the growing demand for materials that are lightweight, nontoxic, and environmentally sustainable. Unlike traditional shielding materials, such as lead, which pose significant health and environmental risks, advanced glasses emerge as a promising alternative. By combining high shielding efficiency with a reduced ecological footprint, these materials represent a forward-looking solution for diverse radiological applications.

Figure 5 presents a keyword network map generated from studies on radiation shielding, highlighting the connections between the main terms and concepts in this research field. The diagram reveals that terms such as "radiation shielding," "glass," and "gamma rays" are central, underscoring their prominence in studies related to radiation protection. The lines connecting the terms represent the frequency and intensity of relationships between topics, illustrating how diverse areas of knowledge, such as "mass attenuation coefficients," "neutrons," and "optical properties," are interconnected. This analysis of keyword interactions provides valuable description into research trends and reveals how various concepts converge to support the development of advanced radiation-shielding technologies and materials.

Figure 5 – The network map of the most frequently used keywords in radiation shielding studies highlights circles representing the most common terms in the literature, where the circle size corresponds to the frequency and relevance of each keyword. The connecting lines illustrate the relationships and interconnections between different concepts explored in the research. The color-coded clusters represent distinct thematic areas, such as radiological protection, shielding materials, and optical properties, emphasizing the multidisciplinary nature of this field. The analysis was conducted in April 2024.

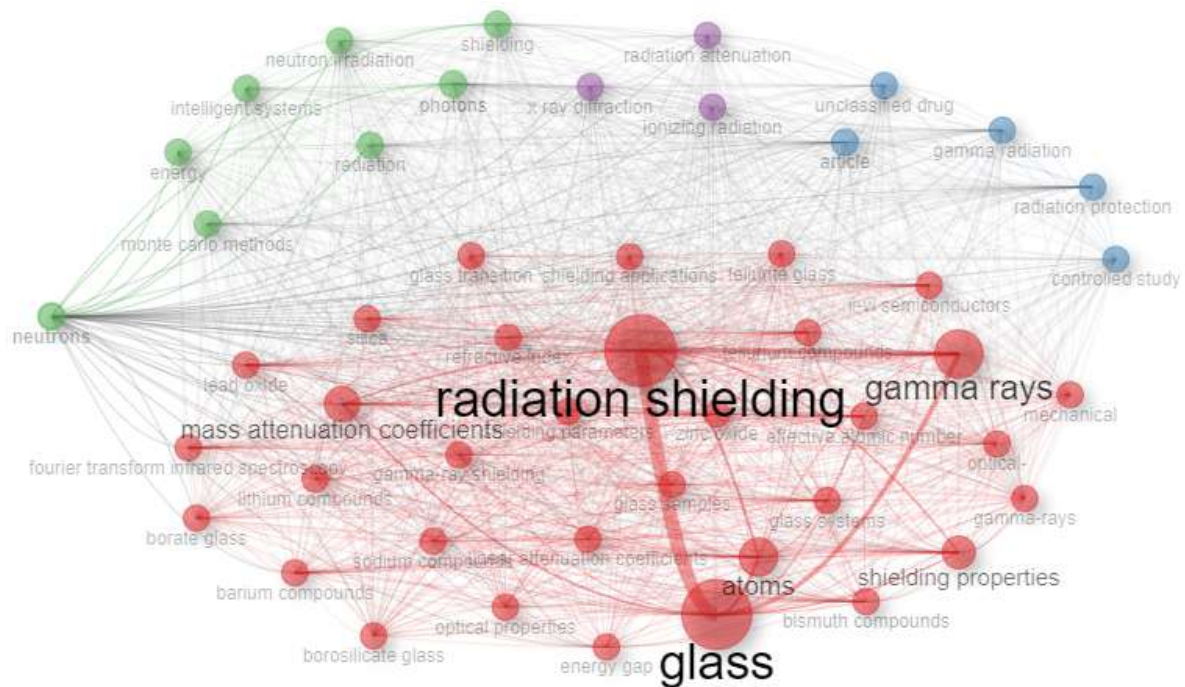


Figure 6 presents a word cloud that highlights the 100 most frequent keywords in research on radiation shielding and glasses. This visualization provides a comprehensive overview of the field, showcasing dominant themes and trends that shape current advancements. Central keywords such as "radiation shielding," "glass," and "gamma rays"

underscore the critical role of radiological protection in various applications, ranging from medical imaging to industrial processes.

The associated terms, including "mass attenuation coefficients," "shielding properties," and "neutrons," highlight the methodological diversity and the range of radiation types studied within this field. These terms reflect ongoing efforts to deepen the understanding of radiation-material interactions, which is essential to improve the efficiency and reliability of shielding technologies. Furthermore, keywords like "bismuth compounds," "lead oxide," "tellurium compounds," and "zinc oxide" signify a strong research focus on developing innovative materials that enhance radiation absorption and attenuation. These advances aim to meet modern demands for sustainability and safety without compromising shielding performance.

This emphasis on material innovation aligns with the urgent need for alternatives to traditional shielding materials such as lead, which pose significant environmental and health risks. By exploring compounds such as bismuth and tellurium, researchers are advancing toward efficient, eco-friendly solutions that maintain or exceed the protective qualities of conventional materials. These developments not only improve the efficacy of shielding, but also align with sustainability goals, reflecting the multidisciplinary and forward-looking nature of radiation shielding research.

The word cloud also reveals the interconnectedness of various research areas. Terms such as "optical properties" and "neutrons" emphasize the dual goals of optimizing material transparency for protective windows and improving radiation absorption for shielding applications. This integration of physics, materials science, and engineering demonstrates how collaborative innovation drives progress in this field.

Furthermore, the analysis highlights the evolving challenges in the development of advanced shielding materials. The prominence of terms related to environmentally friendly and lead-free alternatives underscores the growing emphasis on sustainability. This trend reflects the field's dedication to balancing high performance, safety, and minimal environmental impact, positioning radiation shielding research at the forefront of modern materials science.

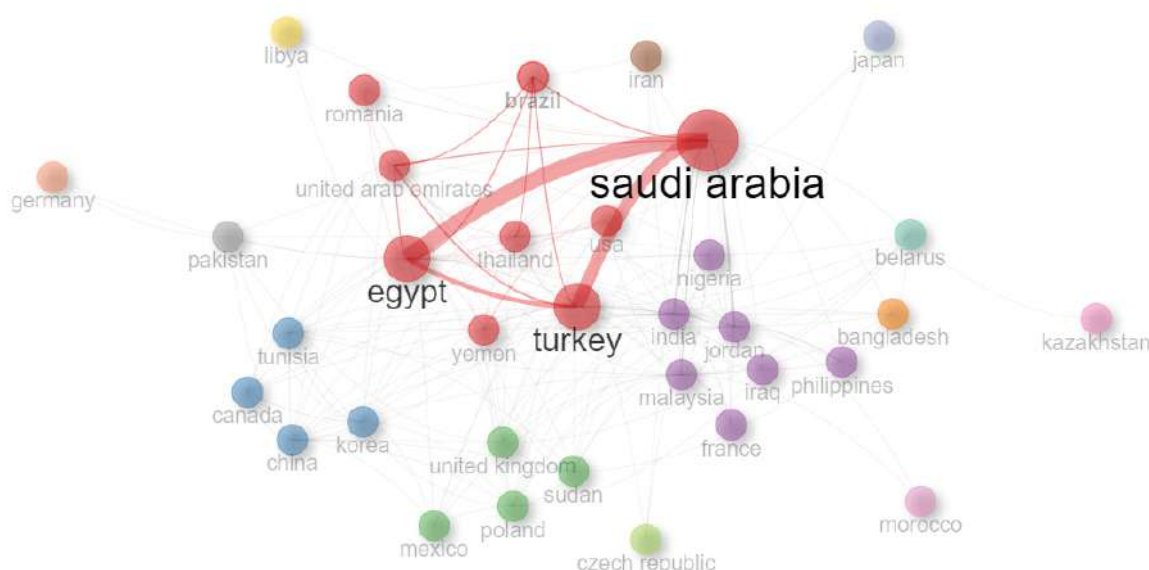
Figure 7 illustrates the scientific collaboration network of Brazil with other countries in the field of radiation shielding in glasses. The map highlights significant partnerships, particularly with nations such as Saudi Arabia, Egypt, and Turkey, which are prominent leaders in research on materials for radiological protection.

When the term "tellurite glasses" is included in the analysis, a notable reduction in the number of publications is observed, indicating that specific research on tellurite glasses for radiation shielding remains an emerging area with significant potential for growth. This scarcity underscores an opportunity to expand studies and foster international collaboration in this innovative field of research.

Despite the limited literature focusing on tellurite glasses, the past decade has



Figure 7 – The international scientific collaboration network emphasizes Brazil connections with other countries in research on radiation shielding in glasses. Key collaboration partners, including Saudi Arabia, Egypt, and Turkey, are highlighted, reflecting Brazil active role in fostering global advancements in this field. The analysis was conducted in April 2024.

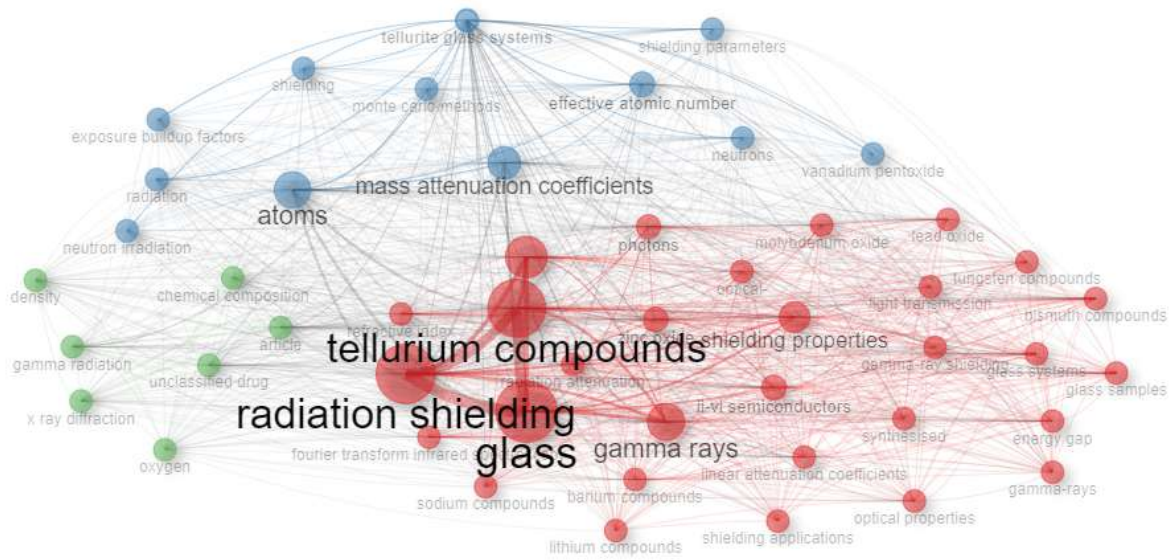


witnessed substantial growth in research dedicated to radiation shielding materials. This surge reflects the increasing demand for new materials with enhanced radiation attenuation properties, driven by the requirements of the healthcare, industrial applications, and security sectors. Furthermore, this progress aligns with global priorities, such as sustainable development and the pursuit of technological innovation.

Figure 8 illustrates the connections between the keywords most frequently used in studies that include "tellurite glasses" as a focus. The diagram reveals the intricate

relationships and interactions between key concepts associated with tellurite glasses and their applications in radiation shielding. Alongside terms like "radiation shielding," "glass," and "gamma rays," other significant keywords such as "tellurium compounds," "mass attenuation coefficients," and "shielding properties" emerge as central themes. These terms highlight the relevance of tellurite glasses in radiological protection. The color-coded clusters reflect distinct thematic areas, such as optical properties, chemical composition, and attenuation coefficients, showcasing the interdisciplinary and innovative nature of this research domain.

Figure 8 – The diagram highlights the main keywords in studies of tellurite glasses for radiation shielding. Connections illustrate the frequency and relationships between terms, with the circle sizes representing their relevance. The color-coded clusters denote distinct thematic areas, including shielding properties, chemical composition, and optical properties. Analysis conducted in April 2024.



2.3.1 SHIELDING PARAMETERS

An investigation of new materials for radiation shielding begins with understanding the parameters used to evaluate them for this purpose. In this section, we will present the main parameters studied and reported in the literature. The attenuation of X-rays and gamma rays follows an exponential behavior, where a monoenergetic radiation beam with initial intensity I_0 passes through an absorbing material of thickness x . The relationship is given by:

$$I = I_0 e^{-\mu x} \quad (2.1)$$

Here, I is the intensity of transmitted radiation and μ is the linear attenuation coefficient, which quantifies the probability of a photon being absorbed or scattered as it

traverses the material. Mathematically, the linear attenuation coefficient (LAC) μ can be expressed as:

$$\mu = \frac{1}{x} \ln \frac{I}{I_0} \quad (2.2)$$

The mass attenuation coefficient (MAC) is used to compare the effectiveness of different shielding materials by normalizing the linear attenuation coefficient by the density of the materials ρ :

$$MAC = \frac{\mu}{\rho} \quad (2.3)$$

This parameter is widely used in the selection of shielding materials as it allows evaluating the effectiveness of the materials independently of their density. Materials with high MAC values, such as lead and tungsten, are frequently used in radiation shielding because of their high attenuation capacity for X-rays and gamma rays. Lead, for example, is widely used in protective barriers in radiology rooms and in portable personal protective equipment (PPE), such as lead aprons and gloves.

Beyond MAC, parameters such as the half-value layer (HVL) and the tenth-value layer (TVL) are crucial for shielding design, as they determine the necessary thickness of the material to reduce incident radiation to safe levels. These parameters are calculated by:

$$HVL = \frac{0.693}{\mu} \quad (2.4)$$

and

$$TVL = \frac{2.302}{\mu} \quad (2.5)$$

The transmission rate (TR) and radiation protection efficiency (RPE) are essential to evaluate shielding performance. TR quantifies the fraction of photons that penetrate the material, while RPE measures the percentage of radiation attenuated:

$$TR(\%) = e^{-\mu x} \times 100 \quad (2.6)$$

and

$$RPE(\%) = (1 - e^{-\mu x}) \times 100 \quad (2.7)$$

The Mean Free Path (MFP) indicates the average distance between two successive photon interactions with the material, serving as an indicator of the effective thickness needed for shielding:

$$MFP = \frac{1}{\mu} \quad (2.8)$$

The effective atomic number (Z_{eff}), or equivalent atomic number, is a parameter used to describe the shielding capacity of materials composed of multiple elements. This parameter is particularly relevant for heterogeneous materials and varies with radiation energy. The Z_{eff} is determined by the atomic cross-section (σ_a) and the electronic cross-section (σ_e):

$$Z_{\text{eff}} = \frac{\sigma_a}{\sigma_e} \quad (2.9)$$

For neutron shielding, the interaction processes and associated parameters differ from those of charged particles. Being neutral particles, neutrons interact primarily through nuclear processes, making them particularly difficult to shield. Fast neutrons with an energy above 1 MeV are not easily absorbed by conventional materials. To attenuate these neutrons, their energy must be reduced to thermal levels, which facilitates their capture by absorber nuclei. This moderation process is crucial as it converts fast neutrons into thermal neutrons through elastic collisions with light nuclei such as hydrogen, carbon, or beryllium, effectively dissipating kinetic energy (Byrne, 2013). Efficient neutron shielding involves using moderators to reduce the energy of fast neutrons, followed by absorber materials to capture the resulting thermal neutrons. To ensure effective shielding in nuclear and radiological applications, a proper combination of moderators and absorbers is required to maximize protection against neutrons in various energy ranges.

Moderators: Materials such as water, paraffin, and polyethylene are used to slow down fast neutrons through elastic scattering, reducing their energy to the thermal spectrum.

Absorbers: After moderation, thermal neutrons are captured by materials such as boron, cadmium, and gadolinium, which have high capture cross-sections.

The fast neutron removal cross-section is a critical parameter for evaluating materials effectiveness against fast neutron shielding. This parameter considers the combined probability of neutron interactions through scattering and capture.

Cross-sections (σ) are fundamental in quantifying the interactions of particles such as neutrons and photons with matter. They represent effective areas of interaction and are used to describe the likelihood of processes such as absorption, scattering, and fission.

Atomic Cross-Section (σ_a): Describes the probability of a neutron being captured by a nucleus, essential in assessing a material's ability to reduce thermal neutron intensity.

$$\sigma_a = \frac{N\mu_m}{N_A} \quad (2.10)$$

where

$$N = \sum_i n_i A_i \quad (2.11)$$

is the total atomic mass of the material components, and N_A is Avogadro's number.

Electronic Cross-Section (σ_e): Relates to the interaction of photons with the electrons of the materials, crucial to determining the effective atomic number (σ_a):

$$\sigma_e = \frac{1}{N_A} \sum_i \frac{f_i A_i}{Z_i} (\mu_m)_i \quad (2.12)$$

These cross-sections are fundamental in evaluating the effectiveness of materials in absorbing and scattering radiation. They provide insights into the probability of interaction between radiation and the material, which is critical for the design and selection of shielding materials in various applications, particularly those involving complex and composite materials where individual atomic contributions to attenuation must be considered.

When the radiation beam is not collimated but broad (wide beam), the Beer-Lambert equation needs to be adjusted to include the photon buildup factor:

$$I = BI_0 e^{-\mu x} \quad (2.13)$$

where B is the buildup factor, which is divided into exposure buildup factors (EBF) and energy absorption buildup factors (EABF). These factors account for the contribution of scattered radiation, which is particularly relevant in environments with complex geometries.

Advancements in technology have led to the development of new materials and techniques to enhance the efficiency of radiological shielding. Innovations include:

- **Composite Materials:** The use of composites such as lead rubber and plastics with metallic particles combines lightness with high attenuation capacity.
- **Nanomaterials:** Inclusion of metallic nanoparticles, such as bismuth and tungsten oxides, in polymer matrices to improve X-ray and gamma absorption.
- **High-Density Alloys:** Heavy-metal alloys, such as tungsten, offer an alternative to lead, combining high density with better mechanical properties and reduced toxicity.
- **Active Shielding:** The use of electromagnetic fields or plasma to deflect or absorb charged particles is an innovative approach in high-radiation environments.

In practice, the selection of shielding material depends on several factors, including:

- **Radiation Energy:** High-atomic-number materials are more effective against high-energy radiation, while hydrogen-rich materials are preferred for neutrons.
- **Available Thickness:** Space constraints may require materials with high density and high attenuation efficiency.

- **Cost and Availability:** The cost and availability of materials are also critical factors that influence choices in industrial and medical settings.

To protect against ionizing radiation, such as X-rays, gamma rays, and neutrons, radiation shielding requires a deep understanding of various attenuation parameters. These parameters include MAC, which indicates the ability of a material to absorb radiation based on its mass; the HVL, which is the thickness required to reduce the radiation intensity by half; and (Z_{eff}) , which reflects the effectiveness of materials in interacting with radiation. Additionally, knowledge of interaction cross-sections, such as the absorption cross-section (σ), is crucial for selecting materials that efficiently capture particles. This is particularly important in applications involving neutrons, where nuclear processes are dominant. These requirements are essential for designing protective barriers that ensure safety and optimize material usage.

2.3.2 Enhanced Radiation Shielding with Tellurite Glasses

As highlighted in Section 2.3, tellurite glasses have emerged as highly promising materials for shielding against ionizing radiation, due to their unique properties, such as high density, compositional flexibility, and excellent optical performance. These characteristics allow for the integration of various modifiers, enabling the fine-tuning of their properties to address specific demands in radiological protection. Recent studies underscore the potential of tellurite glasses as superior alternatives to traditional shielding materials, offering significant advantages in both performance and versatility. This section delves into key findings from recent research.

M.Y. Hanfi et al. examined the binary $\text{TeO}_2\text{-MgO}$ system, employing the Monte Carlo code (MCNP-5) to simulate the theoretical radiation shielding performance of these glasses (Hanfi et al., 2021). Among the compositions tested, the TM10 sample exhibited the highest linear attenuation coefficient (LAC) at low photon energy (0.343 MeV), achieving a value of 0.711 cm^{-1} , compared to 0.584 cm^{-1} for the TM45 sample at the same energy. This demonstrates the superior initial attenuation capacity of the TM10 sample. However, as the gamma photon energy increased, the LAC for TM10 gradually declined, decreasing from 0.711 cm^{-1} to 0.259 cm^{-1} in the energy range of 0.343 to 1.406 MeV. This behavior aligns with the general trend observed in radiation shielding materials, where attenuation efficiency diminishes at higher energies due to reduced photoelectric interaction.

Furthermore, the half-value layer ($D_{0.5}$) for TM10 increased from 0.975 cm at 0.343 MeV to 2.681 cm at 1.406 MeV, indicating its effectiveness in reducing the intensity of radiation at varying energy levels. These results highlight the potential of tellurite glasses for not only efficient attenuation of low-energy photons but also their adaptability across

a broad energy spectrum, further solidifying their role as viable alternatives in advanced radiation shielding applications.

Complementing these findings, Ilyas Çağlar et al. studied binary tellurite glasses modified with oxides such as Nb_2O_5 , B_2O_3 , ZnO , GeO_2 , WO_3 , MoO_3 , and V_2O_5 , prepared via the melting and quenching method (Çağlar et al., 2021). The systems $\text{TeO}_2\text{-B}_2\text{O}_3$, $\text{TeO}_2\text{-Nb}_2\text{O}_5$, $\text{TeO}_2\text{-GeO}_2$, $\text{TeO}_2\text{-MoO}_3$, $\text{TeO}_2\text{-ZnO}$, and $\text{TeO}_2\text{-V}_2\text{O}_5$ were analyzed for their mass attenuation coefficients (MAC) and interactions with gamma rays at 662, 1173, and 1332 keV, emitted by ^{137}Cs and ^{60}Co sources.

In the $\text{TeO}_2\text{-B}_2\text{O}_3$ system, increasing B_2O_3 content (15–35 mol%) improved MAC due to a higher TeO_2 proportion, which increased the density. However, the low atomic number of boron ($Z = 5$) limited Z_{eff} , reducing efficiency compared to systems with higher Z modifiers. The $\text{TeO}_2\text{-Nb}_2\text{O}_5$ system exhibited lower MAC at 662 keV with increasing Nb_2O_5 but showed improved attenuation at higher energies due to enhanced Compton scattering, indicating intermediate performance optimized for high-energy gamma rays. The $\text{TeO}_2\text{-GeO}_2$ system displayed reduced MAC at 662 keV but increased values at 1173 and 1332 keV, leveraging the density of the system despite the moderate atomic number of Ge ($Z = 32$).

The $\text{TeO}_2\text{-MoO}_3$ system showed a significant improvement at higher energies due to Mo ($Z = 42$), a moderate Z element with good gamma-ray absorption capabilities, particularly at medium and high energies. Meanwhile, the $\text{TeO}_2\text{-ZnO}$ system exhibited moderate behavior, with the MAC increasing at higher energies due to density effects and Compton scattering, making it comparable to glasses containing lower Z modifiers. Conversely, the $\text{TeO}_2\text{-V}_2\text{O}_5$ system showed lower efficiency at low energies due to the low Z of vanadium ($Z = 23$) but improved performance at higher energies, making it suitable for specific applications.

M.I. Sayyed et al. evaluated TeO_2 -based glasses over a broad photon energy range (1 keV to 1 GeV) using the WinXcom program (Sayyed, 2016). The study focused on MAC, Z_{eff} , and effective electron density (N_{eff}). Among the compositions, the $\text{TeO}_2\text{-WO}_3$ glasses stood out with high MAC values at low energies, surpassing standard concretes and silicate glasses in gamma-ray shielding. tungsten ($Z = 74$) in the WO_3 modifier significantly improved Z_{eff} , ensuring superior absorption at high photon energies. Additionally, these glasses demonstrated effective neutron shielding, with removal cross-sections varying based on oxide composition, further highlighting their versatility.

G. Susoy investigated nine $\text{B}_2\text{O}_3\text{-TeO}_2$ glasses with varying compositions (Susoy, 2020). Samples with a higher tellurium content exhibited superior shielding properties, including lower mean free path (MFP), half-value layer (HVL), and tenth-value layer (TVL), especially at low energies dominated by the photoelectric effect. The high density and increased Z_{eff} contributed to improved photon absorption, underscoring the efficiency of these glasses in environments that require effective protection against ionizing radiation.

In addition to binary systems, ternary tellurite glasses demonstrate excellent radiation shielding performance, offering the ability to fine-tune properties based on added components. For example, Jamila S. Alzahrani et al. investigated the $\text{TeO}_2\text{-Na}_2\text{O-TiO}_2$ (TNT) glass system (Alzahrani et al., 2021). Their results showed that the linear attenuation coefficients (LAC) vary significantly with photon energy, being highest at lower energies (0.015 keV) where the photoelectric effect dominates, and gradually decreasing with increasing energy due to Compton scattering and pair production. The TNT-E glass, containing the highest TiO_2 concentration, exhibited the highest LAC values, while TNT-A, devoid of TiO_2 , had the lowest. Similarly, the mass attenuation coefficients (MAC) followed a comparable trend, with high values at low energies and a decline as the energy increased. At higher energies, TNT-E outperformed due to its higher TiO_2 content, while TNT-A, with its higher Na_2O content, was more effective at low energies. Furthermore, the mean values of the free path (MFP) and half-value layer (HVL) were the lowest in TNT-E, indicating superior shielding efficiency, particularly at energies greater than 1 MeV. This study underscores the critical role of the density and composition of the glass in determining its radiological protection capabilities.

Another significant ternary system is $\text{TeO}_2\text{-ZnO-Na}_2\text{O}$, studied by M.S. Al-Buriahi et al., who investigated how the substitution of ZnO with Na_2O influences the radiation attenuation properties (Al-Buriahi et al., 2022). The high density of tellurium combined with ZnO resulted in a significantly improved MAC and LAC, essential for effective shielding, although with a decrease in Z_{eff} . The TeZnNa glasses showed variable MAC and LAC values depending on the photon energy, with the TeZnNa3 glass achieving the highest values between 0.284 MeV and 1.333 MeV due to its optimized chemical composition and higher mass density. Furthermore, TeZnNa3 exhibited the lowest HVL, indicating excellent shielding capacity, and the lowest MFP, signifying greater photon interaction. This glass also demonstrated superior performance in fast neutron shielding, achieving the highest removal cross-section (Σ_R), making it an effective neutron moderator and outperforming concrete and commercial glasses.

Further studies by Al-Buriahi et al. investigated systems like $\text{BaO-TeO}_2\text{-WO}_3$ (BTW), $\text{BaO-TeO}_2\text{-Y}_2\text{O}_3$ (BTY), $\text{BaO-TeO}_2\text{-Sr}$ (BTSr), and $\text{BaO-TeO}_2\text{-Li}_2\text{O}$ (BTLi) (Al-onizan et al., 2023). Their findings showed that MAC values decrease with an increase in photon energy due to the dominance of the photoelectric effect at lower energies. The correlation between LAC and MAC across different energies highlighted the significant influence of absorption edges and component densities on radiation absorption capabilities. Among these systems, BTW glass, characterized by its higher density, exhibited the lowest MFP, establishing itself as the most efficient radiation barrier. These results confirm the importance of optimizing density and composition factors in the development of high-performance shielding materials.

Furthermore, Al-Buriahi et al. explored the $\text{TeO}_2\text{-Ag}_2\text{O-WO}_3$ system, demonstrat-

ing that increasing the concentrations of Ag_2O and WO_3 leads to higher density and, consequently, enhanced radiation shielding properties (Al-Buriah et al., 2020b). The mass attenuation coefficient (MAC) values were elevated at low photon energies due to the dominance of the photoelectric effect and decreased as energy increased, consistent with Compton scattering processes. Among the samples, the TAW-D glass exhibited the best radiation attenuation capacity, evidenced by its lower half-value layer (HVL) and mean free path (MFP) values. This superior efficiency, when compared to conventional shielding materials such as concrete and commercial glasses, was attributed to the inclusion of high-atomic-number elements, such as silver ($Z = 47$) and tungsten ($Z = 74$). These elements significantly enhance interactions with photons across a broad energy spectrum, underscoring their role in improving radiation shielding performance.

Another notable ternary system was investigated by R. El-Mallawany et al., who studied zinc-lithium tellurite glasses with varying ZnO concentrations (El-Mallawany et al., 2020). Using simulations with the Monte Carlo Geant4 code, the shielding properties of these glasses were analyzed. TLZ20 glass, containing 20% ZnO , demonstrated the best shielding capacity among all samples. The increased ZnO concentration resulted in significantly improved MAC values and reduced HVL and MFP, highlighting the positive impact of ZnO on shielding efficiency. Despite the lower atomic number of zinc ($Z = 30$) compared to tellurium ($Z = 52$), its contribution to density and structural stability proved crucial in optimizing radiological protection.

In another study, Imheidat et al. examined the $x\text{MoO}_3$ -[70-x] TeO_2 -20BaO-10SrO system, comparing experimental results with theoretical predictions using XCOM software for radiation sources ^{137}Cs (0.661 MeV) and ^{166}Ho (0.184, 0.280, 0.710 and 0.810 MeV) (Imheidat et al., 2022). The findings revealed a strong agreement between the experimental and theoretical values, with relative differences ranging from 0.55% to 2.90% for BSTM0 glass and less than 6% for other samples. In particular, replacing TeO_2 with MoO_3 led to a decrease in glass density, which negatively affected the linear attenuation coefficient (LAC). Additionally, LAC exhibited an exponential reduction with increasing photon energy, reaffirming the dependence of radiation attenuation on both energy and composition. These results underscore the importance of MoO_3 in modulating shielding properties, offering flexibility in the design of glasses for specific radiological applications.

M.S. Al-Buriah et al. studied TCBC glasses containing TeO_2 at concentrations ranging from 20 wt% to 40 wt%, demonstrating that increasing the TeO_2 content improves the glass density and significantly improves the gamma radiation shielding properties (Al-Buriah et al., 2020a). Simulations performed with Geant4 and Phy-X/PSD revealed a decrease in the mass attenuation coefficient (MAC) with increasing photon energy, identifying distinct interaction regions dominated by the photoelectric effect, Compton scattering, and pair production. Among the samples, the TCBC5 glass, with the highest TeO_2 concentration, exhibited the lowest half-value layer (HVL) and mean free path (MFP)

values, confirming its superior shielding performance compared to traditional concretes and commercial glasses.

In a related study, Sayyed et al. investigated the 50TeO₂-10GeO₂-20ZnO-10BaO-10Bi₂O₃ system, which demonstrated exceptional efficiency in gamma radiation absorption (Sayyed et al., 2020). This glass composition achieved some of the highest MAC values, ranging from 0.041 to 66.00 cm²/g, attributed to the high concentration of Bi₂O₃. Furthermore, the system presented the lowest HVL and MFP values, further reinforcing its effectiveness as a shielding material. The high ^{**effective atomic number (Z_{eff})**}, which ranged between 28.73 and 46.19, played a crucial role in the enhancement of gamma radiation interactions, solidifying its superiority over other compositions studied.

Sk Rezaul Karim et al. analyzed the X-ray attenuation properties of TeZnCaB glasses using a diagnostic X-ray machine operating in the 50–120 kVp range (Karim et al., 2024). Their findings indicated that increasing the TeO₂ concentration improved the glass attenuation capacity, as evidenced by reductions in both the HVL and the equivalent lead thickness (LET). The TeZnCaB45 sample, which contains 45% TeO₂, demonstrated shielding performance comparable to a 1.5 mm lead layer, as recommended by the India Atomic Energy Regulatory Agency. This result underscores the potential of TeZnCaB glasses for medical and diagnostic applications, offering a viable, lead-free alternative for radiological protection.

Recently, Burak Berke Solak et al. investigated the compositions of B₂O₃, PbO, TeO₂, and CeO₂, evaluating their shielding capabilities against gamma radiation and neutrons (Solak et al., 2024). The addition of WO₃ to the glasses had a significant impact on photon absorption and neutron capture, resulting in shielding efficiency comparable to PbO-based glasses. With radiation absorption properties superior to those of many commercial materials, these glasses show potential as replacements for conventional shielding glasses in various applications.

Beyond traditional tellurite glass systems, alternative compositions utilize the addition of tellurium to enhance their shielding properties. Y.S. Rammah et al. investigated the germanate-tellurite system in GTGPr1-GTGPr4 glasses, identifying GTGPr4 (10.5GeO₂-72.9TeO₂-16.7Ga₂O₃-0.3Pr₆O₁₁) as the most effective in terms of shielding performance (Rammah et al., 2020b). This glass exhibited high MAC values at low photon energies, particularly around 0.03181 MeV, due to the K absorption edge of tellurium. These values gradually decreased at higher energies, demonstrating effective attenuation across the spectrum. Furthermore, GTGPr4 presented the lowest HVL values, underscoring its capacity to reduce radiation intensity with minimal thickness. The Z_{eff} ranged from 43.07 to 48.19 at 0.04 MeV and between 18.70 and 21.25 at 1.5 MeV, indicating a robust interaction with low-energy radiations. Furthermore, this glass excelled in fast neutron attenuation, confirming its superiority among the studied samples.

Another notable system, 10SrO-(40-x)B₂O₃-30TeO₂-20BaO, was analyzed both

experimentally and theoretically using the XCOM software (Dwaikat et al., 2021). The optimal composition, which contains 15 mol% MoO_3 , achieved an experimental MAC of $0.163 \text{ cm}^2/\text{g}$ at 0.28 MeV, which closely aligns with the theoretical value of $0.160 \text{ cm}^2/\text{g}$. At 0.71 MeV, both values converged at $0.722 \text{ cm}^2/\text{g}$, demonstrating consistent performance. This composition also recorded the lowest HVL and MFP values, indicating superior efficiency as a compact shielding material compared to standard glasses such as RS235 and RS360.

Xinyu Zhao et al. explored B_2O_3 - TeO_2 - BaO glasses doped with heavy metal oxides (Bi_2O_3 , WO_3 , CdO , MoO_3) (Zhao et al., 2024). Among these, the S1 glass, containing Bi_2O_3 , exhibited the highest density (5.266 g/cm^3) and superior photon absorption capacity, particularly at low energies due to the photoelectric effect. The Z_{eff} values followed the order $\text{S1} > \text{S2} > \text{S3} > \text{S4}$, confirming the dominance of S1 in radiation shielding. With its lower HVL, higher radiation protection efficiency, and superior PbE (lead equivalence), S1 exceeded the performance of other commercial materials, meeting stringent protection standards. Moreover, S1 demonstrated the highest fast neutron removal cross-section (FNRCs), outperforming concrete and graphite, validating its dual effectiveness in shielding both gamma rays and fast neutrons.

These studies underscore the transformative impact of integrating tellurium into various glass bases, such as germanates, borates, and heavy oxides. By combining high density, elevated Z_{eff} , and precise compositional modifications, these glasses exhibit exceptional shielding capabilities, meeting the rigorous demands of medical, industrial, and research applications.

Finally, glass systems with alternative formers and the inclusion of tellurium and other components demonstrate significant potential for optimizing shielding properties. Jiale Wu et al. investigated the MAC of B_2O_3 - MnO_2 - CdO glasses across the energy range of 1.5×10^{-2} – 10^3 MeV, revealing a decreasing trend of μ_m with increasing photon energy and notable peaks at the absorption edges of manganese (Mn) and cadmium (Cd) (Wu et al., 2023). The S5 glass, characterized by a higher concentration of CdO , exhibited the highest Z_{eff} , correlated with its superior photon absorption capabilities. With the lowest HVL and TVL values, the S5 glass demonstrated superior shielding efficiency, positioning it as a viable replacement for commercial shielding glasses in medical and nuclear applications.

M.I. Sayyed et al. explored the substitution of BaO with B_2O_3 in PNBB glasses, resulting in increased molar weight and density, which significantly improved the performance of the gamma radiation shielding (Sayyed et al., 2024). The substitution led to an increase in LAC and a decrease in HVL, effectively reducing photon transmission. Among the compositions, PNBB25 displayed performance comparable to that of RS-360 glass, containing 45% PbO , highlighting the PNBB glasses as an effective and environmentally safer alternative for radiation shielding.

N. Intachai et al. studied sodium borosilicate glasses doped with gadolinium (Gd_2O_3), varying concentrations from 0 to 15 mol% (Intachai et al., 2022). The inclusion of Gd_2O_3 increased glass density, refractive index, Z_{eff} and N_{eff} , enhancing the interaction with photons. Although MAC decreased with higher gamma energies, the glasses excelled in photon absorption at lower energies, underscoring their suitability for radiological shielding applications.

Samer E'layan Alawaideh et al. evaluated glasses doped with metal oxides (CaO , TiO_2 , CuO) for their density and shielding properties (Alawaideh et al., 2024). Among the tested systems, the glasses BBZCu doped with CuO exhibited the highest density, LAC, and lowest HVL, significantly outperforming glasses doped with TiO_2 and CaO . BBZCu demonstrated superior gamma radiation absorption at energies ranging from 0.033 to 2.506 MeV, attributed to its higher Z_{eff} and electron density.

These studies highlight how diversifying glass compositions with different formers and dopants, including tellurium, gadolinium, and cadmium, expands the potential for developing high-performance materials. The integration of heavy elements into unconventional glass matrices enables the creation of efficient and tailored materials for radiation protection in a broad range of medical, industrial, and nuclear applications.

3 MATERIALS AND METHODS

3.1 SAMPLE PREPARATION

The samples were prepared in the facilities of the Grupo de Propriedades Eletrônicas e Vibracionais em Materiais (GPEViM) at UEPG. The oxide raw materials used in the synthesis were TeO_2 (Sigma-Aldrich, 2N 99.99%), Na_2CO_3 (Sigma-Aldrich, 99.5%), TiO_2 (Vetec, 99.5%), Li_2CO_3 (Lafan, 99%), MoO_3 (Vetec, 99.5%), BaO (Vetec, 99.5%), and ZnO (Alfa Aesar, 99.99%), all expressed in molar percentages. The detailed compositions of the studied samples are presented in Chapters C and 4.

The glasses were synthesized using the conventional melt-quenching method under ambient atmospheric conditions. This process involves melting the raw materials in a platinum crucible at high temperatures, followed by rapid cooling in stainless steel molds to form the glassy state. The precise amounts of reagents were precalculated to obtain 8 grams of each sample. The oxides were weighed using a precision balance with a sensitivity of 10^{-4} g and then mixed and homogenized in an agate mortar for one hour.

The homogenized mixture was transferred to a platinum crucible and subjected to a controlled heating process on an EDGCON F-1800 furnace. The heating profile is illustrated in Figure 9. Initially, the furnace temperature was increased at a rate of $3^\circ\text{C}/\text{min}$ until reaching 400°C , where it was held for 60 minutes. This step facilitated the calcination process, removing organic impurities. Subsequently, the temperature increased at a rate of $6^\circ\text{C}/\text{min}$ until reaching the melting point, approximately 900°C . The mixture was kept at this temperature for 30 minutes to ensure complete melting and homogenization.

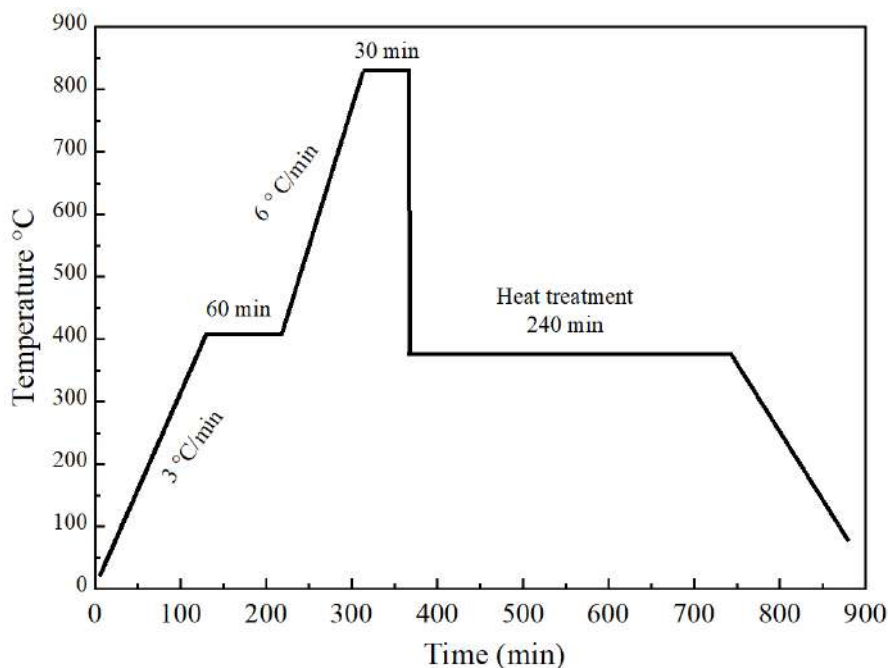
The molten material was then poured into preheated brass molds kept at approximately 250°C . The samples were annealed at this temperature for 4 hours to minimize residual mechanical stresses caused by thermal shock. After the annealing process, the furnace was allowed to cool to room temperature at its natural cooling rate, further alleviating stresses introduced during vitrification.

Once cooled, the glass samples were cut, ground, and polished according to the requirements of subsequent analytical techniques. These post-processing steps ensured uniform sample dimensions and surface quality, which is essential for accurate characterization.

3.2 X-RAY DIFFRACTION

X-ray diffraction (XRD) measurements were conducted using a Rigaku Ultima IV diffractometer at the Complexo de Laboratórios Multiusuários (C-Labmu) of UEPG. The samples were ground and sieved to achieve particle sizes smaller than $53\text{ }\mu\text{m}$. The

Figure 9 – Heating Ramp Used in the Sample Melting Process.



diffractograms were acquired in θ - 2θ mode using the Bragg-Brentano geometry. The X-ray source operated at 40 kV and 30 mA with a copper target ($\text{CuK}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$).

Data collection was carried out with an initial angle (i - θ) of 5° and a final angle (f - θ) of 60° , using a continuous scanning mode. The scan rate was set to $1^\circ/\text{min}$, with a step size of 0.02° . These parameters ensured high-resolution data suitable for analysis of the amorphous nature of the glass samples.

3.3 SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)

The images were acquired by scanning electron microscopy (SEM) with a Tescan VEGA3 system at the Universidade Tecnológica Federal do Paraná (UTFPR), Ponta Grossa campus. Chemical composition analysis was performed through energy dispersive spectroscopy (EDS) with a coupled Oxford Instruments detector, also using the Tescan VEGA3 system. The SEM analysis was performed at a magnification of $1000\times$, operating at a voltage of 20 kV and a working distance of 15 mm.

To prepare the samples, a Quorum SC7620 sputter coater was used to deposit a thin metallic layer under high vacuum on the surfaces of non-conductive samples. To enhance electrical conductivity, a palladium coating was applied for 60 seconds at a current of 15 mA and a voltage of 20 kV. This process ensured optimal imaging and accurate EDS analysis by minimizing the effects of charging on the sample surface.

3.4 DENSITY, MOLAR VOLUME, AND OXYGEN PACKING DENSITY (OPD)

The density of the samples was determined using the Archimedes method. Measurements were performed with a Shimadzu balance (Model AY220) with a precision of 10^{-4} g, located at the *Complexo de Laboratórios Multiusuários (C-Labmu)* in UEPG. First, the mass of each sample was measured in air (m_R). Then, the apparent mass (m_A) of the samples was recorded while submerged in the chosen liquid.

To ensure accuracy, three measurements were taken for the real mass (m_R) and the apparent mass (m_A) for each sample. The density (ρ_g) was then calculated using a specific formula, considering the relationship between the mass in the air, the apparent mass and the density of the immersion liquid.

$$\rho_g = \left(\frac{m_R}{m_R - m_A} \right) \rho_L \quad (3.1)$$

where m_R is the real mass, m_A is the apparent mass, and ρ_L is the density of distilled water (0.9978 g/cm^3). A complete description of the density calculation can be obtained from the following reference (Gunha et al., 2022).

From the density data, the molar volume (V_m) was determined using the following equation:

$$V_m = \left(\frac{M_{W_g}}{\rho_g} \right) \quad (3.2)$$

where M_{W_g} represents the molar mass of the glass, expressed for a molar percentage (mol). Based on the literature, from the values of ρ and V_m , it is also possible to calculate the oxygen packing density (OPD) using the following equation (Dimitrov; Sakka, 1996):

$$OPD = 1000C_0 \frac{\rho_g}{M_{W_g}} \quad (3.3)$$

where $C_0 = (1 - x - y)q + xs + yu$ is the number of atoms per oxygen in the oxide, and q , s , and u represent the number of oxygen atoms associated with each cation, corresponding to each atom (Dimitrov; Komatsu, 2010; Dimitrov; Komatsu, 2015).

3.5 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC tests were performed using a Shimadzu thermal analyzer, model DTG-60, belonging to the *Laboratório de Radiação e Materiais Vítreos (LRMV)* at the *Universidade Estadual de Maringá (UEM)*, Goioerê campus. The non-isothermal process (direct measurement method) was carried out on powder samples with a particle size of less than $< 53 \text{ }\mu\text{m}$. Measurements were taken with a heating rate of $10 \text{ }^\circ\text{C/min}$ from room

temperature to 600 °C. The samples were analyzed in alumina crucibles under a nitrogen atmosphere, with a flow rate of 20 ml/min, using approximately 25 mg of sample.

3.6 RAMAN SPECTROSCOPY

Raman spectroscopy measurements were performed using a Horiba spectrophotometer, model XPLORA, belonging to the *Complexo de Laboratórios Multiusuários* (C-Labmu) at the *Universidade Estadual de Ponta Grossa* (UEPG). The equipment utilized an excitation laser with a wavelength of 532 nm, a grating of 1200 lines/mm, and a coupled microscope with a 50X objective lens and a numerical aperture of 0.40. Measurements were performed in bulk samples, in the range of 100 to 1500 cm^{-1} , with an integration time of 5 seconds.

3.7 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) measurements were conducted at the *Complexo de Laboratórios Multiusuários* (C-Labmu) of the *Universidade Estadual de Ponta Grossa* (UEPG) using a Shimadzu spectrophotometer, model IR-Prestige 21. The measurements were performed in an absorption mode in the range of 400 to 4000 cm^{-1} , with 64 scans and a resolution of 4 cm^{-1} . For the analysis, the samples were ground and sieved to obtain particle sizes smaller than $<53 \mu\text{m}$. A small portion of each sample was dispersed in KBr (potassium bromide) pellets and pressed using a uniaxial press at a pressure of 80 kN.

3.8 OPTICAL ABSORPTION

The optical properties were quantified using a PerkinElmer spectrophotometer, model UV-VIS-NIR Lambda 1050, belonging to the *Grupo de Física dos Materiais* (GFM) of the *Universidade Federal de Goiás* (UFG). For this technique, the samples, approximately 300 μm thick, were optically polished. The measurement range analyzed was from 280 to 800 nm.

3.9 OXIDE ION POLARIZABILITY

From the data obtained for the band gap and the molar volume, it is possible to calculate the average electronic polarizability values of the oxide ions ($\eta_{\text{O}^{2-}}$), based on the relationship presented by Dimitrov and Sakka. According to the literature (Dimitrov;

Sakka, 1996), the behavior of the polarizability of electronic ions is given by the following formula:

$$\eta_{O2-}(E_g) = \left[\frac{V_m}{2.52} \left(1 - \sqrt{\frac{E_g}{20}} \right) - \sum p\eta_i \right] (q)^{-1} \quad (3.4)$$

where η_i is the polarizability of the cation, V_m is the molar volume, and p and q denote the number of cations and oxide ions, respectively, in the chemical formula A_pO_q .

In this work, this relationship was expanded to apply to a ternary system with the general nomenclature $XA_pO_q-YB_rO_s-ZC_tO_u$, where X, Y and Z represent the molar fractions of each oxide. Thus, Equation 3.4 includes V_m as the molar volume of the sample, $\sum \eta_i$ as the molar polarizability of the cations, given by $Xp\eta_A + Yr\eta_B + Zt\eta_C$, and $(q)^{-1}$ as the number of oxide ions in the chemical formula, calculated as $Xq + Ys + Zu$. The molar polarizability of the cations, $\sum \eta_i$, was estimated using cation polarizability data available in the literature (Dimitrov; Sakka, 1996).

3.10 VICKERS MICROHARDNESS MEASUREMENTS

Vickers microhardness measurements were performed using a Leica commercial microhardness tester, model VM HT MOT, located at the Universidade Tecnológica Federal do Paraná (UTFPR), Ponta Grossa campus. For each sample, a series of three measurements was performed under a load of 3 N, and the average hardness of the samples was calculated. The Vickers hardness, H_v , was determined using the following equation:

$$H_v = 1.8544 \frac{P}{d^2} \quad (3.5)$$

where P is the applied load and d represents the average of the impression diagonals (C:1327-15, 2019; Meyers; Chawla, 2008).

3.11 OPTICAL MICROSCOPY

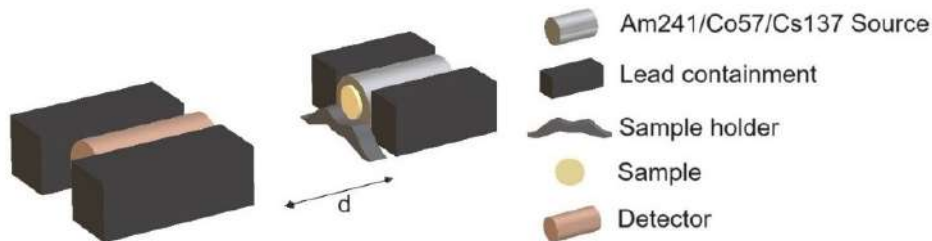
Optical microscopy (OM) images were acquired using a Zeiss microscope, model A2.m, located at the Centro Multiusuário de Caracterização em Pesquisa e Desenvolvimento de Materiais (C²MMa) at UTFPR. The equipment is equipped with an image acquisition system (AxioVision) for microstructural characterization coupled with the microscope. This system includes a digital camera and a computer, enabling the photographic recording of visualized images at magnifications of up to 1000 $\times$ and accommodating samples with a height of up to 25 mm.

3.12 SHIELDING PARAMETERS

An experimental setup was established for radiation shielding measurements using isotopic sources and a NaI(Tl) detector (Ludlum, model 44-2) with appropriate lead shielding and beam attenuation. The experiments were conducted at the *Laboratório de Radiação e Materiais Vítreatos* (LRMV) of the *Universidade Estadual de Maringá* (UEM), Goioerê campus. The sources ^{241}Am and ^{57}Co were encased in lead shields, leaving only the detector direction exposed to minimize background noise and improve the signal-to-noise ratio. Additional lead shielding was placed between the source and the detector to further attenuate the radiation beam.

The distance (d) between the source and the detector was optimized to minimize measurement errors and was set at approximately 15 cm. For the attenuation measurements, the radiation beam was passed through glass samples with thicknesses ranging from 2 to 5 mm. Data acquisition involved recording counts per second (*cps*) as a function of the thickness of the samples placed between the source and the detector. Each measurement was performed for 180 seconds and repeated three times for each sample to ensure precision. The recorded data were analyzed using a pulse height analyzer and a multichannel analyzer (Ludlum model 2000). A schematic of the experimental setup is shown in Figure 10.

Figure 10 – Schematic representation of the experimental setup for ^{241}Am , ^{57}Co , and ^{137}Cs sources, highlighting the alignment of the radiation sources, glass samples, and detector for shielding measurements.



4 RESULTS AND DISCUSSIONS

4.1 PHYSICS, THERMAL, STRUCTURAL AND OPTICAL PROPERTIES

This section presents results of the characterization of tellurite glass matrices designed to optimize the essential properties of radiation shielding. The base compositions used were TeO_2 (65% and 60%) as the former network, ZnO as an intermediate oxide, and Li_2O , Na_2O , TiO_2 , MoO_3 , and BaO as modifiers. Table 2 details the composition and nomenclature of the samples, while Figure 11 shows a photograph of the prepared samples.

A visual inspection reveals notable differences between the samples. Glasses modified with Li, Na, and Ba exhibit a yellowish tint, with the Na-doped sample being the most transparent. The Mo-containing glass shows a yellow-red hue, consistent with the chromatic contribution of MoO_3 . Meanwhile, the Ti-doped samples display a gray color, expected due to the transition metal characteristics of TiO_2 .

Table 2 – Nomenclature and Composition of the Prepared Samples.

Samples	Composition (mol%)						
	TeO_2	ZnO	Li_2O	Na_2O	BaO	TiO_2	MoO_3
65TZLi	65	20	15	-	-	-	-
60TZLi	60	25	15	-	-	-	-
65TZNa	65	20	-	15	-	-	-
60TZNa	60	25	-	15	-	-	-
65TZBa	65	20	-	-	15	-	-
60TZBa	60	25	-	-	15	-	-
65TZTi	65	20	-	-	-	15	-
60TZTi	60	25	-	-	-	15	-
65TZMo	65	20	-	-	-	-	15
60TZMo	60	25	-	-	-	-	15

ZnO exhibits dual functionality in the TeO_2 - Li_2O - ZnO (TLZ) system, acting as a network former in ZnO -rich compositions and as a modifier when its concentration decreases. This dual role allows fine-tuning of glass network connectivity and non-bridging oxygen (NBO) content, significantly influencing polarizability and thermal stability. These properties are critical to improving radiation absorption and thermal resistance (Novatski et al., 2019; Piazzetta, 2015).

Studies indicate that BaO -modified glasses are particularly effective in gamma radiation shielding due to the high atomic number and density of barium, but their performance in neutron absorption is limited (Alzahrani et al., 2022; Amat et al., 2021; Wu et al., 2023). In contrast, glasses containing MoO_3 provide a balanced shielding capacity for both photons and neutrons. This is attributed to the high density and structural

Figure 11 – Photograph of the samples subjected to analysis.



complexity of MoO_4 units, which improve network connectivity. Nevertheless, further refinement is necessary to optimize neutron absorption.

The results of microstructural, physical, and thermal analyses of these glasses are discussed in detail, focusing on the relationship between the network structure and the optical/thermal properties. These insights aim to guide the development of advanced glass matrices that combine the benefits of existing compositions while addressing their limitations. The goal is to create versatile materials suitable for high-radiation environments.

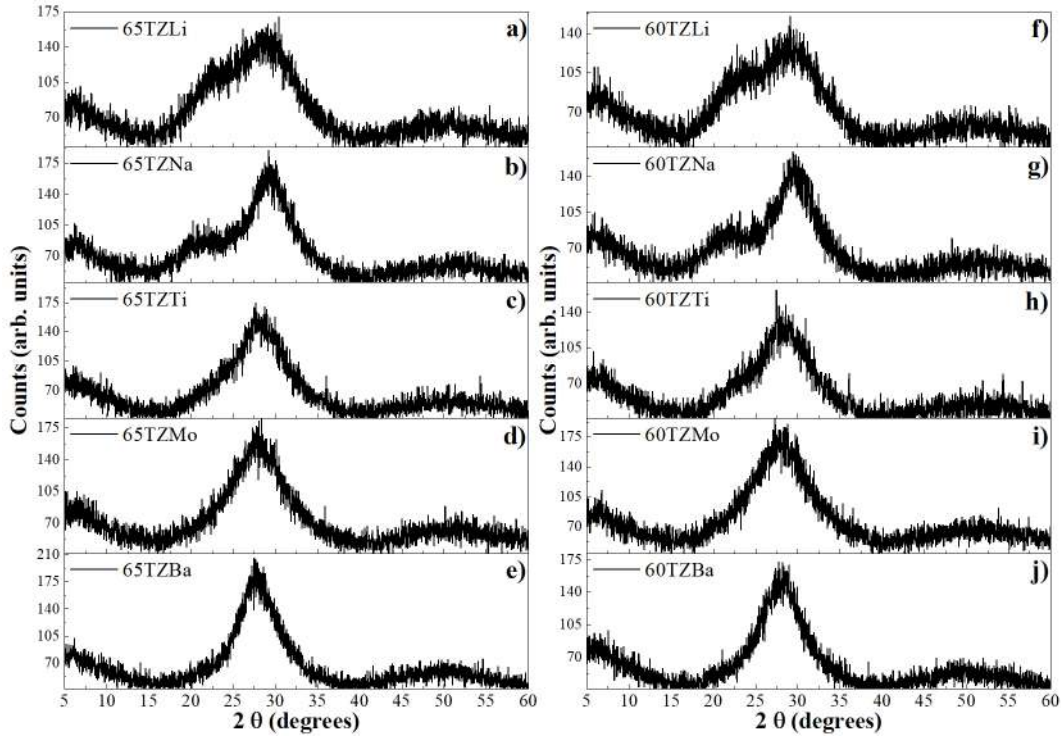
4.1.1 XRD and EDS

The X-ray diffractograms presented in Figure 12 confirm the amorphous nature of the samples, characterized by the absence of well-defined diffraction peaks. The addition of modifiers and intermediates did not induce any observable structural changes, strengthening the consistency of the amorphous matrix (Hosseini; Souiri, 2022; Strutynski et al., 2022; Ahmmad et al., 2012; Kilic et al., 2021). Surface morphology analysis of optically polished samples was conducted using SEM, with the results detailed in Appendix D.

Chemical surface analysis was performed by EDS on an area of $100 \mu\text{m}$, as shown in Figure 13 ¹. Figure 13 provides the percentage distribution of each element along with color mapping for the 65TZMo sample, offering a comprehensive visualization of the elemental distribution on the surface.

¹ The EDS measurement is considered qualitative due to several factors: spectral resolution, matrix effects, excitation and ionization factors, peak overlap, calibration and standards, and detection limits. Due to these limitations, EDS is primarily used to qualitatively identify elements in a sample, providing quick and straightforward information about elemental composition. For precise and detailed quantifications, more advanced and specific analytical techniques are required

Figure 12 – X-ray diffraction patterns of the samples with modifier and intermediate oxides, highlighting the structural influences of the different components analyzed in the study.



The EDS spectral results confirm the presence of Te, O, Zn and Mo in the 65TZMo sample, with elemental composition percentages summing to 100 wt%. As expected, Li_2O was not undetected in Figures 58 and 62 due to instrumental limitations, necessitating qualitative comparisons for these components (see Appendix D). In particular, the close agreement between the theoretical and experimental values in all samples indicates minimal material loss during synthesis and successful homogenization of the glass matrix, as detailed in Chapter 3.

4.1.2 Physical Properties

The physical properties of the synthesized tellurite glasses, such as density, molar volume (V_M), molar mass, and oxygen packing density (OPD), were determined using the Archimedes principle, as detailed in Section 3.4. Table 3 presents these parameters, essential for understanding structural organization and physicochemical behavior (Sayyed; Lakshminarayana, 2018). Variations in density arise from compositional changes that influence atomic arrangements and interatomic distances within the glass network, while OPD quantifies the efficiency of ionic packing by representing the number of oxygen atoms per unit volume.

The addition of modifying oxides plays a critical role in altering the physical properties of glasses. Li_2O , for example, acts as a structural modifier by disrupting TeO_4

Figure 13 – EDS spectral map and elemental distribution for the 65TZMo sample, showing the distribution of Te, O, Zn, and Mo on the materials surface.

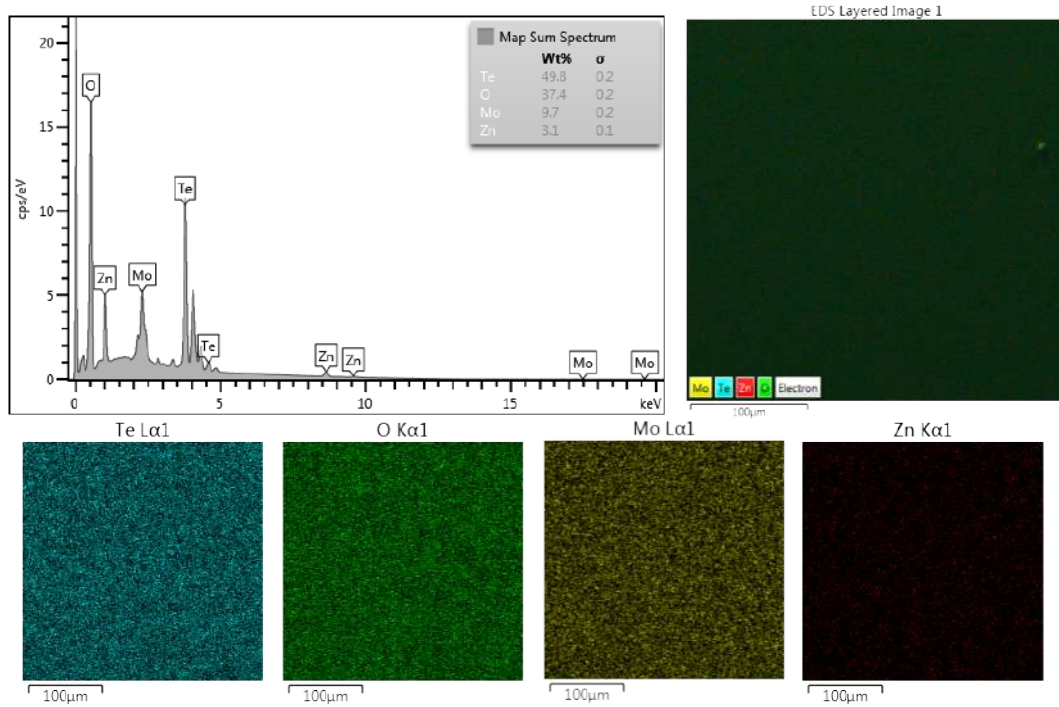


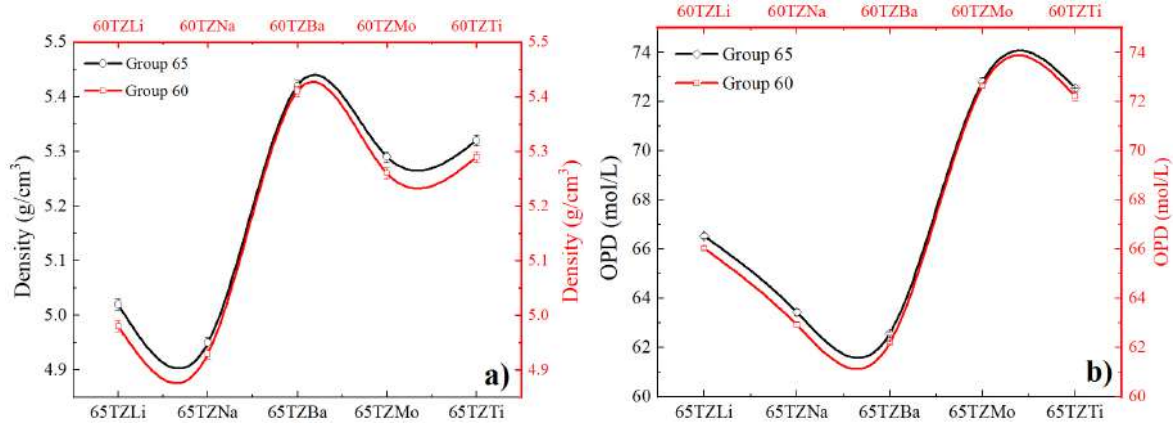
Table 3 – Physical and thermal properties of the synthesized glass samples, highlighting density, molar volume, and OPD variations as a function of composition.

Sample	ρ (g/cm ³)	M (g/mol)	V_M (cm ³ /mol)	OPD (mol/L)	$T_g \pm 2$ °C	$T_x \pm 2$ °C	ΔT	$T_p \pm 2$ °C
65TZLi	5.023 ± 0.009	124.50	24.79 ± 0.05	66.5 ± 0.12	260	362	102	376
60TZLi	4.978 ± 0.007	120.59	24.22 ± 0.04	66.05 ± 0.08	263	360	97	338
65TZNa	4.977 ± 0.006	129.31	25.98 ± 0.03	63.50 ± 0.03	275	335	60	354
60TZNa	4.928 ± 0.009	125.40	25.45 ± 0.05	62.9 ± 0.10	277	344	67	357
65TZBa	5.418 ± 0.001	143.01	26.40 ± 0.01	62.51 ± 0.01	337	458	121	490
60TZBa	5.404 ± 0.005	139.10	25.74 ± 0.02	62.16 ± 0.05	343	467	124	486
65TZTi	5.320 ± 0.001	132.00	24.81 ± 0.01	72.54 ± 0.01	348	473	125	504
60TZTi	5.290 ± 0.002	128.08	24.21 ± 0.01	72.28 ± 0.03	346	465	119	486
65TZMo	5.281 ± 0.004	141.61	26.81 ± 0.02	72.72 ± 0.05	326	427	101	480
60TZMo	5.263 ± 0.009	137.70	26.16 ± 0.04	72.63 ± 0.08	334	456	122	493

polyhedra and forming non-bridging oxygens (NBO). Its small ionic radius enhances structural compactness, leading to relatively high density and OPD values, consistent with those reported in the literature (Novatski et al., 2019; Tatsumisago et al., 1995; Idalgo et al., 2006; Sekiya et al., 1992; Kalampounias; Boghosian, 2012). In contrast, Na₂O, which has a larger ionic radius, reduces both density and OPD. This reduction is attributed to the increase in the length of the bonds and structural rearrangements within the glass network (Hrabovsky et al., 2024; Manikandan et al., 2012; Hrabovsky et al., 2022; Clermont-Gallerande et al., 2021; Al-Buriahi et al., 2022; Rammah et al., 2020a; Shen; Jha, 2008).

BaO, on the other hand, significantly increases density because of its high molar mass. However, its larger atomic radius expands the interatomic spacing, which reduces OPD and decreases the packing efficiency (Samsonov, 2012; Hrabovsky et al., 2022;

Figure 14 – Density and OPD behavior of the synthesized samples, illustrating the structural effects of modifying oxides and highlighting the similarities between 60% and 65% TeO_2 groups.



Manikandan et al., 2012; Linganna et al., 2020; Hrabovsky et al., 2024; Alzahrani et al., 2022). TiO_2 promotes structural compaction by leveraging the smaller ionic radius of Ti^{4+} , which facilitates tighter packing within the glass matrix. This effect transforms TeO_4 units into TeO_3 or TeO_{3+1} configurations, increasing the presence of NBOs (Zaki et al., 2018; Gunha et al., 2019; Gomes et al., 2018; Kabalci et al., 2011; Almatari, 2019; Laariedh et al., 2020). Similarly, MoO_3 enhances density due to its high molar mass while inducing structural changes. Specifically, it breaks TeO_4 units into TeO_{3+1} configurations, a transformation that increases OPD and highlights the role of Mo in the reorganization of the glass network (Gomes et al., 2018; Alfryyan et al., 2023; Gunha et al., 2024).

Among the samples, those containing Li_2O exhibited moderate OPD values, as shown in Table 3 and illustrated in Figure 14. This behavior is attributed to the smaller ionic radius of Li^+ , which enhances structural compactness while maintaining a balanced oxygen packing density. In contrast, samples with Na_2O demonstrated a reduced density and OPD due to the larger ionic radius of Na^+ , which increases interatomic spacing and bond lengths, resulting in a less compact glass structure.

BaO -containing glasses displayed the highest density values, attributed to the high molar mass of Ba. However, these glasses exhibited lower OPD values, a consequence of the expanded interatomic space associated with the larger atomic radius of Ba, despite its high molar mass (Shen; Jha, 2008). Samples containing TiO_2 and MoO_3 revealed different structural behaviors. Ti^{4+} , with its smaller ionic radius, promoted structural compaction by reducing interatomic distances and transforming TeO_4 units into TeO_3 or TeO_{3+1} configurations. On the other hand, Mo facilitated the formation of NBOs by breaking TeO_4 units into TeO_{3+1} structures, thereby enhancing overall OPD (Kabalci et al., 2011; Almatari, 2019).

Figure 14 illustrates the behavior of density and OPD in different samples, highlighting the impact of modifying oxides on the glass matrix. This correlation further evidences the structural adjustments introduced by each composition.

It should be noted that the comparison between the 60% and 65% TeO_2 groups did

not show significant changes in the values of the physical property. Both groups exhibited similar trends in density, molar volume, and OPD, indicating that the relative proportions of TeO_2 do not substantially alter these parameters within the compositions studied.

These observations are consistent with literature reports. For example, the density values for Na_2O -containing glasses align with reported ranges of 4.80 to 5.35 g/cm^3 , depending on the composition (Shen; Jha, 2008; Al-Buriahi et al., 2022). Similarly, TiO_2 -doped glasses demonstrate densities from 5.31 to 5.49 g/cm^3 , highlighting Ti^{4+} role in compacting the structure (Kabalcı et al., 2011). MoO_3 -based systems show densities around 5.06–5.10 g/cm^3 , with studies attributing these results to the contribution of Mo to structural and optical properties (Liu et al., 2019; Aşkın; Dal, 2019; Gunha et al., 2024).

In general, the interaction between the molar mass, ionic radius, and structural rearrangements underscores the importance of modifying oxides in tailoring the physical properties of tellurite glasses. These findings highlight the potential for the design of materials with optimized properties for specific applications, particularly in radiation shielding and optical systems.

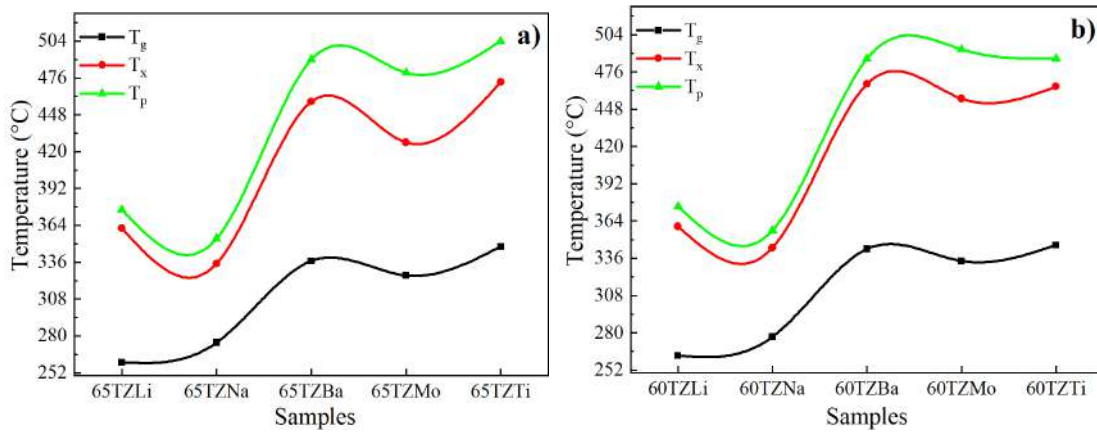
4.1.3 Differential Scanning Calorimetry (DSC) analysis

The DSC analysis provided detailed information on the thermal transitions of the glasses. From the measurements, the glass transition temperature (T_g), the crystallization onset temperature (T_x), the thermal stability parameter (ΔT) and the exothermic crystallization peak (T_p) were determined. These parameters showed significant changes across the modifying oxides, highlighting their influence on the thermal behavior of the glasses. The values for T_g , T_x , and ΔT are presented in Table 3, and their variations are illustrated in Figure 15 for T_g , T_x , and T_p , and in Figure 16 for ΔT . Additional details regarding the DSC curve for the 65TZLi sample can be found in Appendix D.

The glass transition temperature (T_g), which marks the transition from a liquid amorphous state to a rigid solid state, varied notably between samples. Both the 65% and 60% TeO_2 groups exhibited clear trends depending on the modifying oxide. Samples containing TiO_2 and BaO demonstrated higher T_g values, reflecting the formation of a more compact and rigid glass network. For example, 65TZTi and 60TZTi exhibited T_g values of approximately 348 °C and 346 °C, respectively, while 65TZBa and 60TZBa showed T_g values of 337 °C and 343 °C. These results align with previous studies reporting that TiO_2 and BaO enhance OPD and thermal stability through their roles as network formers and modifiers, promoting stronger glass networks (Zaki et al., 2018; Shi et al., 2022).

The samples containing MoO_3 exhibited intermediate T_g values, with 326 °C and

Figure 15 – Glass transition temperature (T_g), onset crystallization temperature (T_x), and crystallization peak temperature (T_p) for the 65% (a) and 60% (b) TeO_2 groups, showing significant changes depending on the modifying oxide, as reported in the literature.



334 °C for 65TZMo and 60TZMo, respectively. This behavior can be attributed to the dual role of MoO_3 as both a network former and a modifier. The presence of MoO_3 promotes partial disruption of the glass network, leading to the formation of non-bridging oxygens (NBOs), while simultaneously contributing to a relatively stable structure due to the formation of Mo-O bonds. These results are consistent with findings that highlight MoO_3 unique role in enhancing thermal stability while maintaining moderate structural flexibility (Alfryyan et al., 2023; Aşkın; Dal, 2019; Gomes Junior, 2015; Gomes et al., 2018; Gunha et al., 2024).

The samples containing Li_2O and Na_2O exhibited distinct behaviors in terms of T_g . Glasses containing Li_2O demonstrated lower T_g values, approximately 260 °C and 263 °C for 65TZLi and 60TZLi, respectively. The smaller ionic radius of Li^+ improves the structural compactness and promotes tighter packing within the glass network. However, the increased ionic mobility associated with Li^+ limits the formation of a highly rigid and thermally stable network. In contrast, Na_2O -containing samples displayed moderate T_g values of approximately 275 °C and 277 °C for 65TZNa and 60TZNa. The larger ionic radius of Na^+ results in increased interatomic distances and increased network flexibility, which reduces thermal resistance and stability (Gunha et al., 2019; Novatski et al., 2019).

These results align with the literature, which highlights Li_2O dual role as a network modifier and compactness enhancer, contributing to moderate thermal stability. Conversely, Na_2O network-disrupting effects are associated with a reduction in structural compactness and thermal resistance due to its larger ionic radius and the resulting increase in non-bridging oxygens (NBO) (Tatsumisago et al., 1994; Shen; Jha, 2008; Novatski et al., 2019).

The onset temperature of crystallization (T_x) exhibited similar trends in the samples, with significant variations based on the modifying oxides. TiO_2 was the most effective at increasing T_x , with values of approximately 473 °C and 465 °C for 65TZTi and 60TZTi, respectively. This behavior underscores TiO_2 critical role in enhancing thermal resistance

and preventing crystallization. Its smaller ionic radius and strong ability to form TeO_3 or TeO_{3+1} units promote a more compact and rigid glass network. Studies have shown that TiO_2 enhances network connectivity by increasing non-bridging oxygen (NBO) units, leading to a glassy matrix with improved thermal stability (Gunha et al., 2019; Ghribi et al., 2015).

BaO followed closely, with T_x values of 458 °C and 467 °C for 65TZBa and 60TZBa. The high molar mass of Ba contributes to an increased glass density, while its role as a network modifier stabilizes the glass structure by filling interstitial spaces and enhancing packing efficiency. Furthermore, the ability of BaO to form a more rigid network by interacting with TeO_4 polyhedra further delays the onset of crystallization. Previous studies confirm that BaO improves the stability and thermal resistance of the glass by increasing the cohesive energy of the network (Shi et al., 2022).

MoO_3 samples exhibited intermediate T_x values of 427 °C and 456 °C for 65TZMo and 60TZMo, respectively. This reflects MoO_3 dual behavior as both a network former and a modifier. Although MoO_3 introduces NBOs by disrupting TeO_4 units, it also stabilizes the network through the formation of Mo–O bonds, which contribute to a partially cohesive structure. The literature highlights that MoO_3 enhances thermal properties by balancing structural flexibility with moderate rigidity, making it effective in applications that require intermediate stability (Dimitrov; Sakka, 1996).

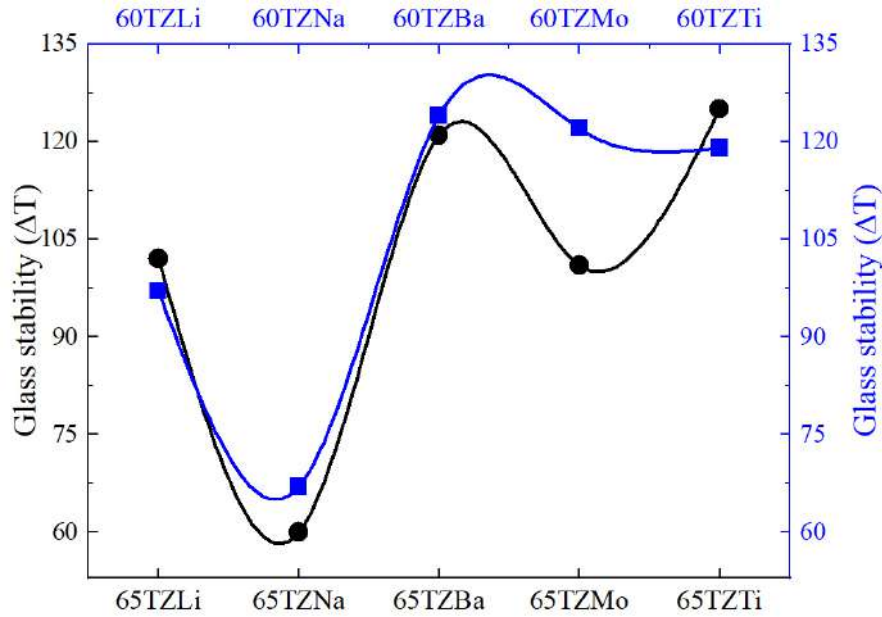
Li_2O -containing glasses displayed moderate T_x values of 362 °C and 360 °C for 65TZLi and 60TZLi, respectively. The smaller ionic radius of Li^+ enables tighter packing and better structural compactness compared to Na^+ . However, the increased ionic mobility associated with Li^+ reduces the rigidity of the glass network, resulting in a balance between stability and flexibility. Studies show that Li_2O introduces moderate stability by promoting compactness while allowing sufficient ion mobility for applications requiring dynamic thermal environments (Dimitrov; Sakka, 1996).

In contrast, Na_2O samples had the lowest T_x values, approximately 335 °C and 344 °C for 65TZNa and 60TZNa. The larger ionic radius of Na^+ increases interatomic distances and introduces significant network flexibility, which reduces compactness and promotes crystallization at lower temperatures. The literature confirms that Na_2O disrupts the glass network by forming a high number of NBO, which weaken the structural integrity and lower the thermal resistance (Dimitrov; Sakka, 1996).

The maximum peak temperature of crystallization (T_p) reflects the highest rate of heat release during crystallization and indicates the resistance of the glass network to complete crystallization. The samples containing TiO_2 , BaO and MoO_3 exhibited the highest values T_p , highlighting their role in enhancing thermal resistance by stabilizing the glass network and delaying crystallization. TiO_2 promotes compactness, BaO increases density and rigidity, and MoO_3 introduces stabilizing Mo–O bonds while maintaining flexibility (Gunha et al., 2019; Shi et al., 2022).

In contrast, Li_2O and Na_2O showed lower T_p values, reflecting reduced thermal resistance. Li_2O high ionic mobility and Na_2O network-disrupting effects, such as increased interatomic distances and the formation of NBO, lead to a greater propensity for crystallization (Dimitrov; Sakka, 1996; Shen; Jha, 2008).

Figure 16 – Thermal stability parameter (ΔT) of the 65% and 60% TeO_2 groups, highlighting the influence of modifying oxides on network compactness and crystallization resistance, consistent with literature trends.



The thermal stability parameter (ΔT) further supports these findings, as illustrated in Figure 16. TiO_2 and BaO exhibited the highest ΔT values, exceeding 125 °C for 65TZTi and 119 °C for 60TZTi, highlighting their ability to form compact and stable glass networks. These results are consistent with the literature that emphasizes the network-forming properties of TiO_2 , which enhances structural compactness, and BaO , which contributes to increased density and stability due to its high molar mass (Gonçalves et al., 2016; Shi et al., 2022).

MoO_3 samples displayed intermediate ΔT values, approximately 101 °C for 65TZMo and 122 °C for 60TZMo, confirming their role in the balance of structural stability and flexibility. This aligns with the findings that MoO_3 , acting as both a former network and a modifier, introduces Mo–O bonds that stabilize the network while maintaining some flexibility, which is critical for applications requiring moderate thermal stability (Alfryyan et al., 2023; Aşkın; Dal, 2019; Gunha et al., 2024).

Li_2O samples showed ΔT values of 102 °C and 97 °C for 65TZLi and 60TZLi, respectively, reflecting moderate stability. This behavior corresponds with literature associating Li_2O with improved structural compactness due to its smaller ionic radius, while its high ionic mobility limits the rigidity of the glass network. Conversely, Na_2O -containing glasses demonstrated the lowest ΔT values, around 60 °C and 67 °C for both 65TZNa and 60TZNa. The literature attributes this to Na_2O larger ionic radius, which disrupts net-

work compactness by increasing interatomic distances and non-bridging oxygens (NBO), coupled with its hygroscopic nature that promotes crystallization (Gunha et al., 2019; Kabalci et al., 2011).

In summary, the DSC analysis revealed significant variations in thermal stability between the modifying oxides for the 65% and 60% TeO_2 groups. These results align with the findings of the literature, reaffirming the roles of TiO_2 and BaO as effective stabilizers, MoO_3 as a balanced modifier, and Na_2O as a destabilizing component in tellurite glass systems.

4.1.4 Structural Properties

The structural properties were analyzed using Raman and Fourier transform infrared (FTIR) spectroscopies. In tellurite glasses, the *Raman-active* vibrational modes are associated with different structural units of pure TeO_2 , characterized by bands centered at 420, 460, 615, 660, 730, and 780 cm^{-1} (El-Mallawany, 2016; Sekiya et al., 1992; Novatski et al., 2019). Based on the glass systems chosen for the substitution of intermediate/modifier oxides, the following vibrational modes were identified:

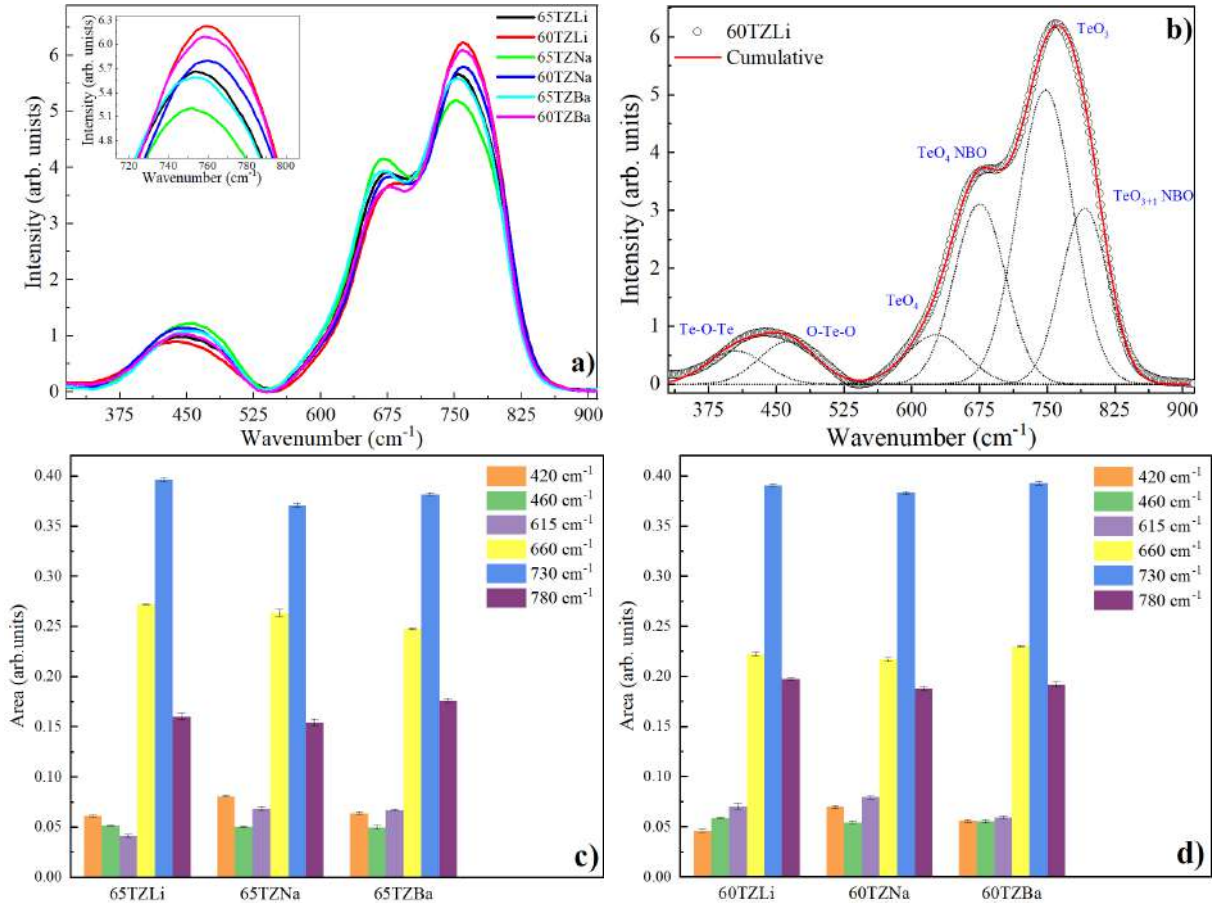
- ✓ **Te–O–Te Bonds:** Vibrational modes around 450 cm^{-1} indicate the presence of TeO_4 units connected by bridging oxygens (BO), which are critical for maintaining network connectivity (Novatski et al., 2019; Gunha et al., 2022);
- ✓ **TeO_4 Units:** Modes at 615 cm^{-1} and 665 cm^{-1} correspond to TeO_4 units without and with non-bridging oxygens (NBOs), respectively. The incorporation of modifier oxides, such as Li_2O , Na_2O , BaO , and ZnO , disrupts Te–O–Te bonds and introduces NBOs, modifying the structural connectivity (Novatski et al., 2019; Alfryyan et al., 2023);
- ✓ **TeO_3 Units:** Bands at 730 cm^{-1} and 780 cm^{-1} are attributed to TeO_3 units with or without NBOs, reflecting a disruption in the glass network caused by the presence of modifier oxides (Hrabovsky et al., 2022; Shen; Jha, 2008);
- ✓ **Te–O–Mo and Mo–O–Mo Bonds:** The incorporation of MoO_3 introduces bands at higher frequencies, such as 875 cm^{-1} , corresponding to MoO_4 and MoO_6 units. These bands highlight molybdenum role in modifying the glass structure by creating new bonds that alter the networks properties (Gomes et al., 2018; Alfryyan et al., 2023; Liu et al., 2019; Linganna et al., 2020);
- ✓ **Te–O–Ti and Ti–O–Ti Bonds:** The addition of TiO_2 results in bands around 351 cm^{-1} and 850 cm^{-1} , corresponding to TiO_4 units. These vibrations confirm TiO_2

role as a network former, enhancing structural connectivity through the formation of new bonds between titanium and oxygen (Gunha et al., 2019; Zaki et al., 2018; Clermont-Gallerande et al., 2020).

Figure 17-a) presents the Raman spectra of samples containing Li, Na, and Ba. The inset of the figure provides a detailed view of the region between 720 and 800 cm^{-1} , highlighting specific vibrational characteristics associated with structural modifications introduced by the modifier oxides. Figure 17-b) shows the Gaussian deconvolution applied to the Raman spectra of the 60TZLi sample, offering a more precise interpretation of the vibrational modes and their contributions to the glass network.

Figures 17-c) and 17-d) illustrate the behavior of the vibrational modes for the 65 and 60 groups, respectively, allowing a comparative analysis of the structural changes caused by the varying compositions. These comparisons emphasize the influence of Li, Na, and Ba on the connectivity and compactness of the tellurite glass network, aligning with the structural trends observed in other studies.

Figure 17 – **(a)** Raman spectra of samples containing Li, Na, and Ba, with a detailed view of the 720–800 cm^{-1} region (inset). **(b)** Gaussian deconvolution of the Raman spectra for the 60TZLi sample, highlighting specific vibrational contributions. **(c)** Comparative analysis of the vibrational modes for 65TZLi, 65TZNa, and 65TZBa samples. **(d)** Comparative analysis of the vibrational modes for 60TZLi, 60TZNa, and 60TZBa samples.



The bands at 420 and 460 cm^{-1} are attributed to the symmetric bending and stretching vibrations of Te–O–Te bonds formed by sharing the vertex of the TeO_4 , TeO_{3+1} and TeO_3 structural units, respectively. These bands are directly related to the connectivity of the glass network. The band at 420 cm^{-1} is influenced by the vibrations of lithium, sodium, and barium cations, each of which interacts with the Te–O–Te bonds in different ways. The addition of Li_2O tends to create non-bridging oxygens (NBOs) by disrupting Te–O–Te bonds, resulting in a more open and flexible network. An increase in the band area is observed when Li_2O is replaced by Na_2O , indicating that the Te–O–Te bonds are maintained or even reinforced (Novatski et al., 2019). Although Na_2O also generates NBOs, the larger ionic radius of sodium compared to lithium promotes a slightly more connected network (Clermont-Gallerande et al., 2021; Gunha et al., 2019; Shen; Jha, 2008). The incorporation of BaO, with its larger and heavier barium ions, further strengthens the glass network by enhancing the connectivity of Te–O–Te bonds. This contributes to greater thermal and structural stability, consistent with findings in other studies (Gonçalves et al., 2016; Manikandan et al., 2012; Linganna et al., 2020).

The band at 460 cm^{-1} is specifically attributed to Te–O bonds, confirming the strengthening of the glass network through an increase in Te–O–Te bonds, which facilitates the formation of TeO_4 units. Incorporation of BaO enhances the intensity of this band, indicating further strengthening of the Te–O–Te bonds due to the higher connectivity provided by the larger and heavier barium ions (Manikandan et al., 2012; Hrabovsky et al., 2022). The substitution of Li_2O with Na_2O and BaO leads to higher band intensities, reflecting the stabilization and strengthening of the glass network. This substitution promotes the formation of a more rigid and interconnected structure, as both Na_2O and BaO contribute to increased network connectivity compared to Li_2O , aligning with previously observed structural trends.

The band centered at 615 cm^{-1} is attributed to the antisymmetric vibration of TeO_4 units. An increase in intensity is observed in samples containing Na_2O , while a decrease is observed in those substituted with Li_2O and BaO. This behavior highlights the distinct structural effects of each modifier. The region around 660 cm^{-1} , associated with the Te–*axOeq*–Te vibrations, shows an increase in intensity with the substitution by Li_2O , consistent with the findings for the TeO_2 –BaO–ZnO system (Gonçalves et al., 2016; Manikandan et al., 2012; Alzahrani et al., 2022; Gunha et al., 2024). In contrast, substitutions with Na_2O and BaO do not produce significant variations in this region. Previous studies have identified an additional vibration band in the Raman spectra of binary TeO_2 –ZnO glasses and ternary tellurite systems, attributed to Zn–O–Zn or Zn–O–Te bridges (Gonçalves et al., 2016; Manning et al., 2012; Manikandan et al., 2012; Sabadel et al., 1997; Gunha et al., 2024). The area of this band decreases in the group containing 60 mol% TeO_2 , likely due to the incorporation of ZnO. The variable ZnO Zn^{2+} , similar to its behavior in silicate glasses, influences the glass structure. At low concentrations, BaO acts

as a network modifier, binding to two NBOs and contributing to good thermal stability. In contrast, when ZnO is present in concentrations greater than 25 mol%, it transitions to acting as a former network, significantly modifying the glass structure (Novatski et al., 2019).

The region around 730 cm^{-1} is attributed to the vibrational modes of TeO_3 units. The intensity of this band decreases with the substitution of Na_2O , indicating a reduction in TeO_3 units likely caused by the formation of non-bridging oxygens (NBO), which reduce network connectivity. In contrast, substitution with BaO results in a slight increase in band intensity, particularly in the 65 group, where the intensity remains relatively stable. This suggests that BaO stabilizes TeO_3 units, maintaining or even improving the connectivity of the glass network. In the 60 group, which contains a higher concentration of ZnO, an increase in TeO_3 units is observed. This behavior is likely due to the formation of Te-O-Zn bonds, leading to the creation of ZnO_4 units that significantly modify the structure of the glass network (Bürger et al., 1992). This phenomenon is consistent with the findings of the literature, which report that ZnO transitions to acting as a network former when incorporated at concentrations greater than 25 mol%, contributing to substantial structural modifications in tellurite glasses (Novatski et al., 2019).

The region around 780 cm^{-1} is attributed to the stretching vibrations of Te-O-(NBO) bonds in the TeO_{3+1} structural units. An increase in the intensity of this band is observed when transitioning from group 65 to group 60, indicating a rise in the number of non-bridging oxygens (NBOs) and, consequently, greater structural disorder within the vitreous network. This behavior is consistent with observations in TeO_2 -BaO- Li_2O and TeO_2 -BaO-ZnO systems, where substitutions with BaO and ZnO improve network connectivity by introducing more NBOs (Gonçalves et al., 2016; Manikandan et al., 2012).

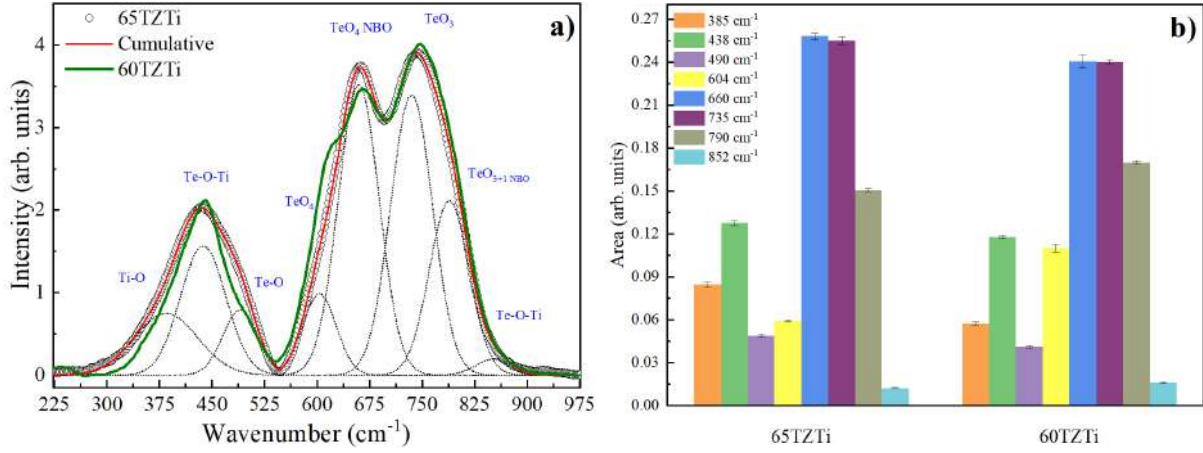
The bands at 420 and 450 cm^{-1} , associated with the bending and stretching vibrations of Te-O-Te bonds formed by units that share TeO_4 , TeO_{3+1} , and TeO_3 units, also exhibit increased intensity. This suggests that Te-O-Te bonds are strengthened and become more dominant, compensating for the reduction in NBO bonds observed in the 730 cm^{-1} region. Consequently, the vitreous network becomes more interconnected and structurally stable with the presence of BaO and ZnO, reinforcing a more rigid and cohesive network structure.

In summary, the substitution of Li_2O with Na_2O and BaO induces significant changes in the structure of the vitreous network. While Na_2O and BaO enhance or maintain Te-O-Te bonds, they contribute to a more stable and interconnected network. These findings are consistent with previous studies that highlight the formation of more cohesive and structurally stable glass networks with the incorporation of specific modifying oxides (Clermont-Gallerande et al., 2021; Hrabovsky et al., 2022).

Figure 18-a) presents the Raman spectra of samples containing Ti, along with the Gaussian deconvolutions applied to these spectra. These deconvolutions provide an

important detailed description of the structural characteristics and chemical interactions within the vitreous matrix. Figure 18-b) illustrates the vibration modes for the 65TZTi and 60TZTi samples, allowing a comparative analysis of the compositions and their respective influences on the structure of the glass network.

Figure 18 – (a) Raman spectra of Ti-containing samples, including Gaussian deconvolutions and the corresponding vibrational modes for the 65TZTi sample. (b) Comparative analysis of vibrational modes for the 65TZTi and 60TZTi samples, highlighting the structural differences between these compositions.



Incorporation of TiO₂ into tellurite glass matrices induces new vibrational bands associated with TiO₂ structural units, significantly modifying the TeO₂ framework. These changes affect Raman bands correlated with TeO₃, TeO₄ and TeO₃₊₁ units, as well as Te–O–Te and O–Te–O bonds. The literature reports the emergence of bands at 385 and 852 cm⁻¹, attributed to TiO₂ units (Gunha et al., 2019; Gupta et al., 2017; Clermont-Gallerande et al., 2020).

The band at 385 cm⁻¹, associated with Ti–O stretching vibrations, indicates interactions between TeO₄ and TiO₂ units. The formation of Te–O–Ti bonds alters the vitreous network, contributing to increased thermal stability (Clermont-Gallerande et al., 2020). A decrease in the intensity of this band for the 60 mol% TeO₂ group suggests that high concentrations of ZnO disrupt the Te–O–Te or Te–O–Ti bridges, favoring Te–O–Zn bonds. This behavior aligns with the findings of Novatski et al., who reported that ZnO enhances connectivity by forming ZnO₄ units, increasing the rigidity of the material and the thermal stability (Novatski et al., 2019).

The 438 cm⁻¹, associated with Te–O–Te bending vibrations, is stabilized by TiO₂, resulting in a more connected network and increased band intensity. Similarly, the band at 490 cm⁻¹, attributed to Te–O–Te bending vibrations, confirms network strengthening through the formation of O–Te–O structures (Clermont-Gallerande et al., 2020; Zaki et al., 2018; Clermont-Gallerande et al., 2020).

The band at 604 cm⁻¹, attributed to antisymmetric vibrations of TeO₄ units, shows a decreased intensity in samples containing TiO₂, probably due to the formation of TeO₃ and Te–O–Ti bonds. These changes reflect interactions between TeO₄ and TiO₆

units, enhancing the rigidity of the network (Clermont-Gallerande et al., 2020; Ghribi et al., 2015; Gunha et al., 2019). In the 60 mol% TeO_2 group, ZnO contributes to the formation of Te-O-Zn bonds, creating a denser and thermally stable network (Zaki et al., 2018; Novatski et al., 2019).

The band at 735 cm^{-1} corresponds to Te-O stretching vibrations in TeO_3 units. The addition of TiO_2 redistributes Te coordination, forming TeO_{3+1} and TeO_3 units, increasing structural complexity. The band at 780 cm^{-1} , attributed to Te-O-(NBO) stretching in TeO_{3+1} units, increases in intensity with TiO_2 addition, reflecting higher structural disorder and NBO formation. This behavior correlates with increased oxygen packing density (OPD), indicating greater network disorder.

The band at 852 cm^{-1} , characteristic of Ti-O stretching vibrations in TiO_4 units, confirms the presence of tetrahedral TiO_2 , which improves the rigidity of the network and the thermal stability (Clermont-Gallerande et al., 2020; Ghribi et al., 2015; Gunha et al., 2019). The addition of TiO_2 leads to the formation of cross-linked Te-O-Ti bonds, significantly improving the connectivity and thermal stability of the network.

Overall, TiO_2 plays a critical role in modifying tellurite glass structure, enhancing network complexity and stability for applications requiring robust, thermally stable materials.

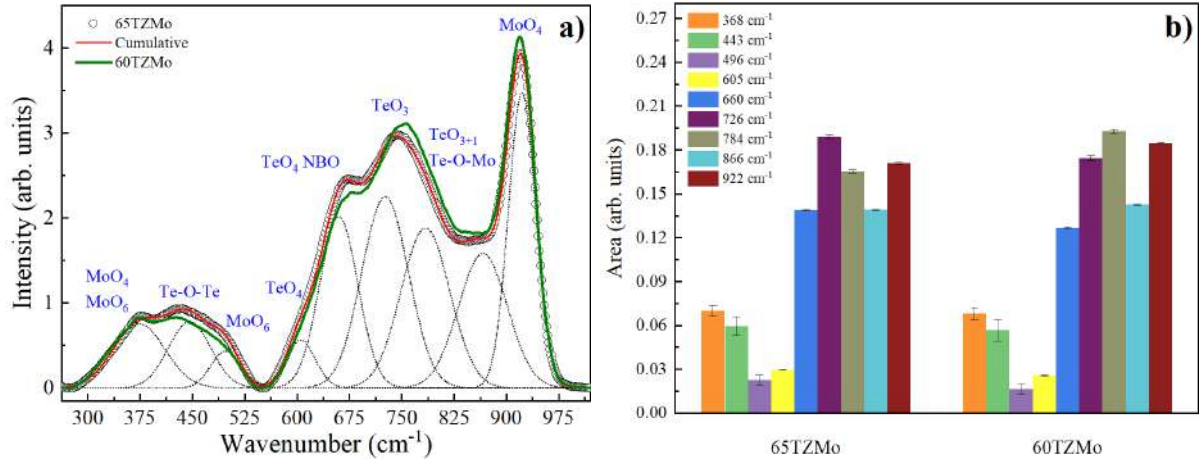
Figure 19-a) presents the Raman spectra of the Mo-containing samples, along with the Gaussian deconvolutions applied to these spectra. These deconvolutions offer an important detailed description of the structural characteristics and chemical interactions within the vitreous matrix. Figure 19-b) illustrates the area of the deconvoluted Raman bands for the 65TZMo and 60TZMo samples, enabling a comparative analysis of the compositions and their impact on the glass network structure.

The addition of MoO_3 significantly increases the intensity of the bands at 660 and 784 cm^{-1} , indicating a higher number of non-bridging oxygens (NBOs) and, consequently, a greater structural disorder within the glass network. The bands at 866 and 922 cm^{-1} confirm the presence of MoO_3 structural units, which enhance the rigidity and thermal stability of the glass. The band at 922 cm^{-1} , specifically attributed to the formation of Te-O-Mo bonds, reinforces network connectivity, resulting in a more interconnected and stable structure.

A detailed analysis of the relative area intensities between the high- and low-frequency bands reveals that increasing the concentration of MoO_3 in the matrix results in a significant reduction in Te-O -related units. This reduction affects the vibrational modes associated with Te-O-Te bonds, which contribute to structural units trigonal bipyramidal (TeO_4) and trigonal pyramidal (TeO_3), both with and without non-bridging oxygens (NBO).

The addition of MoO_3 reorganizes the glass network, leading to the breaking of $\text{Te-}ax\text{O}_{eq}\text{-Te}$ bonds, characteristic of pure TeO_2 . Consequently, a decrease is observed in

Figure 19 – (a) Raman spectra of the Mo-containing samples, including Gaussian deconvolutions and corresponding vibrational modes for the 65TZMo sample. (b) Area analysis of the deconvoluted Raman bands for the 65TZMo and 60TZMo samples, providing a comparative overview of their structural influences.



the bands at 435, 605, 660, 726, and 784 cm^{-1} , which are associated with TeO_2 structural units. MoO_3 incorporation strengthens Te-O-Mo bonds, reflected in the prominent band around 922 cm^{-1} .

In the 784 cm^{-1} region, corresponding to the stretching vibrations of the Te-O-(NBO) bond in the TeO_{3+1} structure, a decrease in intensity reinforces the reduction seen in the 435 cm^{-1} band, where Te-O-Te bonds also diminish. This reduction in NBOs coincides with an increase in MoO_4 and MoO_6 units, leading to a more open and less dense network. This structural transition affects the thermal stability of the system, as evidenced by its thermal properties.

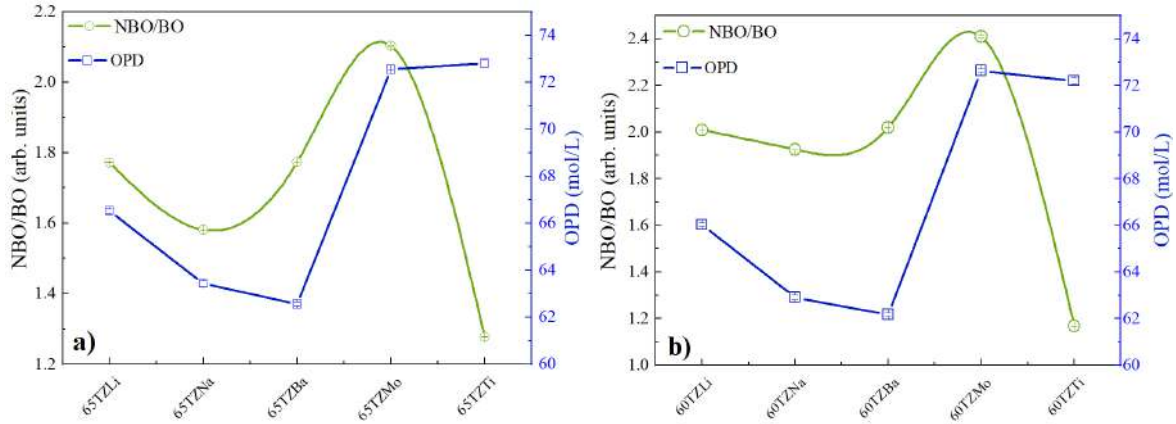
The behavior of MoO_4 and MoO_6 units reflects the intercalation of Mo and Li atoms within a continuous network of structural units. The significant increase in intensity observed in the 866 cm^{-1} band is attributed to the growth of Mo-based structural units and the conversion of NBOs, as Te-O-Te bonds break to form Te-O-Mo bonds. The incorporation of MoO_3 into the glass structure enhances connectivity, creating a less dense but more cohesive network, consistent with observed physical properties and the reduction in NBOs.

These findings align with previous studies, which demonstrate that the addition of MoO_3 improves the thermal and structural properties of tellurite glasses. The incorporation of MoO_3 has been shown to increase the glass transition temperature (T_g) and the onset crystallization temperature (T_x), thereby enhancing the material's resistance to crystallization and overall thermal stability (Liu et al., 2019; Gunha et al., 2024).

The ratio of non-bridging oxygens (NBOs) to bridging oxygens (BOs) in the system can be estimated using the molar ratio $[\text{TeO}_3/\text{TeO}_4]$. This ratio is calculated based on the bands areas at 780, 730, 660, and 615 cm^{-1} , as described in the literature (Himei et al., 1994).

$$\frac{NBO}{BO} = \frac{(2x[O/Te] - 3)x[TeO_3/TeO_4] + 2x[O/Te] - 4}{[O/Te]x([TeO_3/TeO_4] + 1)} \quad (4.1)$$

Figure 20 – Variation in the number of non-bridging oxygens (NBOs) and bridging oxygens (BOs), calculated by the ratio of the band intensities at $780\text{ cm}^{-1} + 730\text{ cm}^{-1}$ (NBO-related bands) over $660\text{ cm}^{-1} + 615\text{ cm}^{-1}$ (BO-related bands), and comparison with the oxygen packing density (OPD), illustrating the evolution of the network structure and connectivity with the incorporation of modifying oxides. **(a)** Group 65; **(b)** Group 60.



The results of Equation 4.1 are presented in Figure 20, illustrating the variation in the NBO/BO ratio between different tellurite glass compositions. The NBO/BO ratio, calculated using the intensities of Raman bands at 780 cm^{-1} , 730 cm^{-1} , 660 cm^{-1} , and 605 cm^{-1} , is a critical parameter that influences the structural and physical properties of the glass. A higher NBO/BO ratio indicates greater structural disorder and an increase in non-bridging oxygens (NBOs), affecting thermal stability, rigidity, and optical properties.

- **Samples with MoO_3 (60TZMo and 65TZMo):** These samples exhibit the highest NBO/BO ratios, indicating significant network disruption and an increase in NBOs. This structural modification enhances the glass ability to accommodate various structural units, improving thermal stability and rigidity. The formation of MoO_4 and MoO_6 units, evidenced by bands at 866 cm^{-1} and 922 cm^{-1} , contributes to a stable and interconnected network.
- **Samples with BaO (60TZBa and 65TZBa):** BaO results in relatively high NBO/BO ratios, albeit lower than MoO_3 . Acting as a network modifier, BaO disrupts the Te-O-Te network and introduces NBOs, improving mechanical properties and resistance to thermal stress. BaO facilitates structural stabilization, as noted in its influence on thermal and mechanical behavior (Bhattacharya; Shashikala, 2019).
- **Samples with Li_2O (60TZLi and 65TZLi):** Samples containing Li_2O show moderate NBO/BO ratios. Li_2O modifies the network by breaking the Te-O-Te linkages and forming Te-O-Li bonds, increasing structural flexibility without significantly compromising rigidity.

- **Samples with Na₂O (60TZNa and 65TZNa):** Na₂O results in moderate NBO/BO ratios, slightly higher than Li₂O. As a network modifier, Na₂O introduces fewer NBOs, maintaining a more interconnected and stable network. However, Na₂O reduces thermal stability and increases the tendency of the materials to crystallize.
- **Samples with TiO₂ (60TZTi and 65TZTi):** TiO₂ produces the lowest NBO/BO ratios. Its dual role as a former and a network modifier contributes to a balance between BOs and NBOs (Zaki et al., 2018). This balance enhances rigidity and thermal stability while maintaining flexibility, which is attributed to the formation of cross-linked Te–O–Ti bonds.

Incorporation of MoO₃ markedly increases the NBO/BO ratio, resulting in a more disordered network with improved thermal and mechanical properties. BaO and TiO₂ introduce NBOs to a lesser extent, but still improve the stability of the network. Li₂O and Na₂O exhibit moderate impacts, with Na₂O favoring a slightly less stable network. These structural variations are pivotal in the tailoring of tellurite glasses for applications in optical devices, radiation shielding, and high-temperature environments.

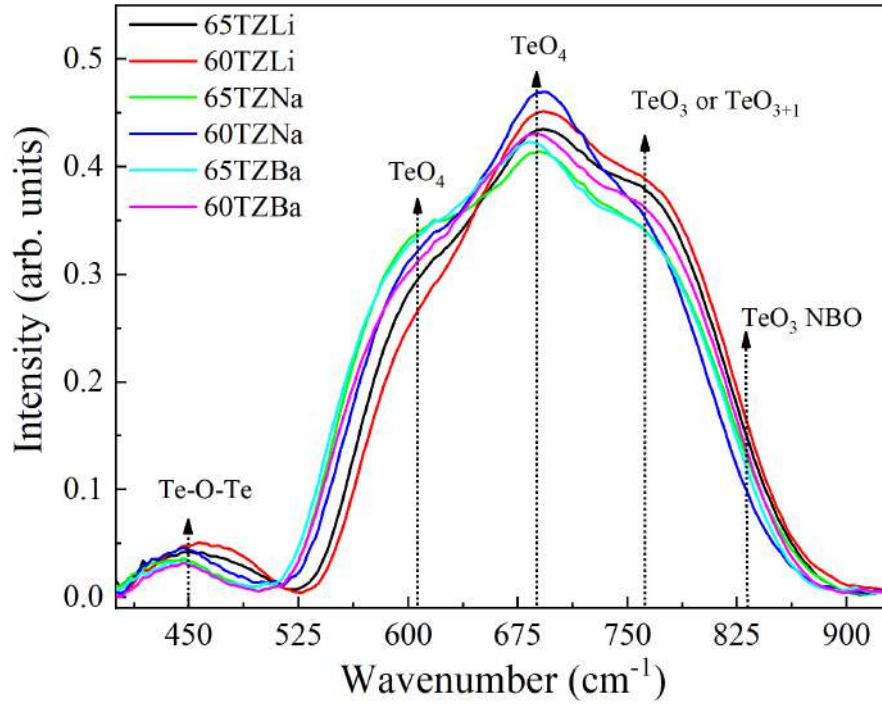
To corroborate the results obtained from the Raman spectra, FTIR measurements were performed to evaluate the vibrational modes of the TeO₂-based glass samples, with the results presented in Figure 21. Typically, TeO₂-based glasses exhibit four distinct vibration modes in FTIR spectra at 450 cm⁻¹, 620 cm⁻¹, 685 cm⁻¹, and 750 cm⁻¹, corresponding to vibrations of TeO₄ units (Sekiya et al., 1992). An additional vibration mode at 830 cm⁻¹ is associated with TeO₃ units containing non-bridging oxygens (NBOs) (Gunha et al., 2022).

The band at 450 cm⁻¹, associated with Te–O–Te vibrations, exhibits a slight decrease in intensity compared to Li-containing samples. This suggests that the addition of modifiers such as Na and Ba reduces these linkages, favoring the strengthening and formation of other structural units. In contrast, the band at 620 cm⁻¹, corresponding to TeO₄ units, shows a significant increase in intensity, indicating enhanced network connectivity through the reduction of simple Te–O–Te linkages and an increase in TeO₄ units (Amat et al., 2021; Sayyed et al., 2023a).

Despite a decrease in the intensities of bands associated with TeO₄ units at 675 cm⁻¹, TeO₃ or TeO₃₊₁ units at 750 cm⁻¹, and TeO₃ units with NBO at 830 cm⁻¹, the 60TZNa sample stands out with an increase in the intensities of these peaks. This behavior is consistent with the NBO/BO ratio, where 60TZNa exhibits the lowest value, while other samples show variations consistent with these findings (Kavaklıoğlu et al., 2015; Çelikbilek et al., 2013).

These variations suggest that the introduction of modifiers induces the conversion of TeO₄ units into TeO₃, accompanied by a reduction in the number of NBO. The differences in the peak intensity reflect variations in the deformation of TeO₄ units. For

Figure 21 – FTIR spectra of TeO_2 -based glasses modified with different oxides (Li, Na, and Ba), highlighting the characteristic vibrational modes of TeO_4 and TeO_3 structural units.



example, Ba promotes a more compact and organized structure due to its larger ionic radius and polarizability, resulting in glasses with higher density (Alfryyan et al., 2023).

Glasses dominated by symmetrical TeO_4 units typically exhibit a primary vibrational mode around 670 cm^{-1} , with a secondary characteristic at 620 cm^{-1} . In contrast, glasses with distorted TeO_4 units show a dominant mode at 620 cm^{-1} and a secondary mode at 670 cm^{-1} (Sidek et al., 2009). The strengthening of the 620 cm^{-1} band highlights significant structural reorganization within the glass, consistent with the results of Raman spectroscopy. These findings underscore the complexity of structural interactions in modified glasses and their dependence on the nature of the modifying oxide.

Figure 22 presents the FTIR spectra of TeO_2 -based glasses modified with TiO_2 and MoO_3 , highlighting the structural changes induced by the addition of these oxides to the glass network.

In Figure 22-a, corresponding to glasses modified with TiO_2 (65TZTi and 60TZTi), the spectra display characteristic peaks at 450 cm^{-1} (Te-O-Te), 620 cm^{-1} and 685 cm^{-1} (TeO_4), 750 cm^{-1} (TeO_3 or TeO_{3+1}), 830 cm^{-1} (TeO_3 with NBO), and an additional peak around 870 cm^{-1} , attributed to Te-O-Ti vibrations. These peaks reflect the incorporation of titanium-containing units into the glass network and the reorganization of TeO_2 structural units.

Incorporation of TiO_2 significantly improves the connectivity of glass networks, as evidenced by the increased intensity of the bands associated with TeO_4 and Te-O-Ti. Titanium primarily acts as a network former, promoting the formation of Te-O-Ti linkages and, at higher concentrations, the development of TiO_4 units. This structural modification

improves the density and stability of the material, consistent with the findings of previous FTIR analyzes, showing that Ti incorporation initially saturates Te–O–Ti interchains before forming independent TiO_4 structural units (Gunha et al., 2019; Stambouli et al., 2012; Shaltout, 2000; Sabadel et al., 1997).

Additionally, the presence of TiO_2 reduces the quantity of non-bridging oxygens (NBOs), as indicated by the NBO/BO ratio. This reduction is reflected in the decreased intensity of bands associated with NBOs, suggesting a reorganization of the network to accommodate titanium. Consequently, a more compact and interconnected structure is formed, improving the structural integrity of the glass and enhancing the interaction between the Te and Ti units (Sabadel et al., 1997; Stambouli et al., 2012).

Figure 22 – (a) FTIR spectra of TeO_2 -based glasses modified with TiO_2 (samples 65TZTi and 60TZTi), highlighting the vibrational modes associated with Te–O–Te, TeO_4 , TeO_3 , and Te–O–Ti bonds. (b) FTIR spectra of TeO_2 -based glasses modified with MoO_3 (samples 65TZMo and 60TZMo), showing the characteristic vibrational modes of Te–O–Mo, TeO_4 , TeO_3 , and MoO_4 structural units.

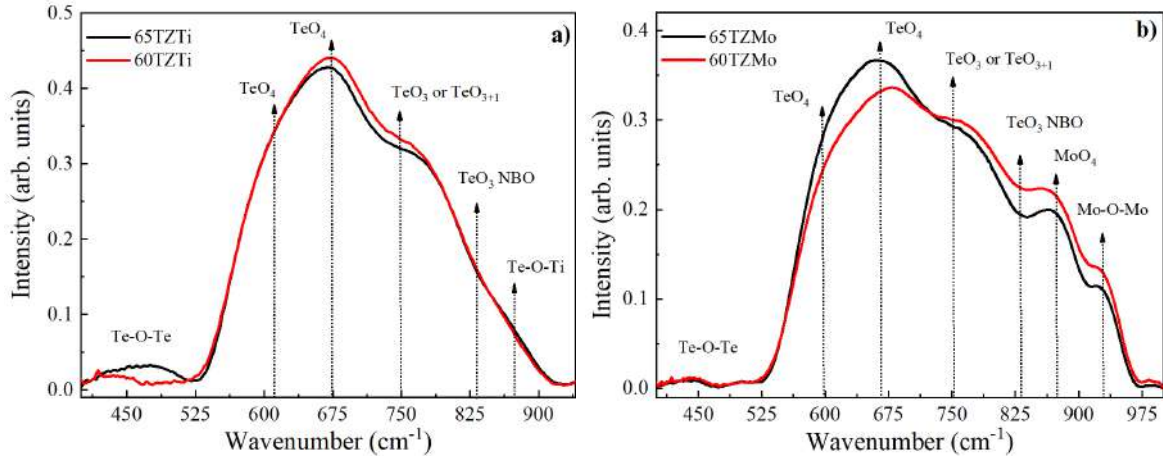


Figure 22-b) presents the FTIR spectra of glasses modified with MoO_3 (65TZMo and 60TZMo). The spectra reveal vibrational modes at 450 cm^{-1} (Te–O–Te), 620 cm^{-1} and 685 cm^{-1} (TeO_4), 750 cm^{-1} (TeO_3 or TeO_{3+1}), and 830 cm^{-1} (TeO_3 with NBO), along with additional peaks between 870 and 950 cm^{-1} attributed to MoO_4 and Mo–O–Mo vibrations. These features highlight the structural role of MoO_3 in the glass network.

The incorporation of MoO_3 promotes the formation of MoO_4 units, which interact with TeO_4 structural units, modifying the glass framework. This interaction increases the local disorder within the network, as evidenced by the enhanced presence of Mo–O–Mo linkages and the introduction of additional NBOs. These structural changes directly influence the thermal and optical properties of the glass, reflecting the dual role of MoO_3 as both a network modifier and a network former. The observed increase in the NBO/BO ratio and OPD values for Mo-modified samples corroborates these findings, demonstrating their greater structural disorder compared to other compositions (Gomes Junior, 2015; Pal et al., 2001; Al-Ani et al., 2006).

The comparison between FTIR spectra of glasses modified with TiO_2 and MoO_3

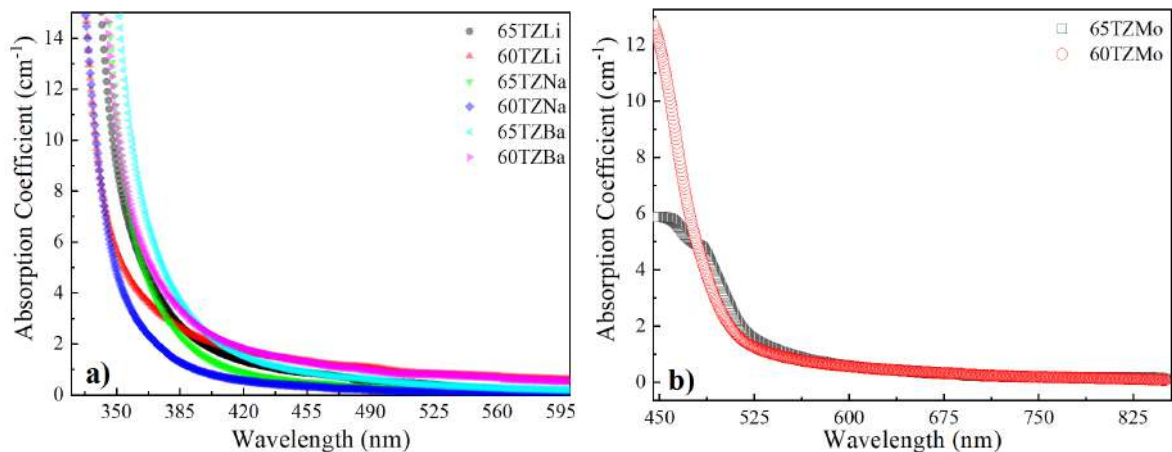
underscores the distinct influences of these oxides on the glass structure. While TiO_2 enhances network connectivity and reduces NBOs, contributing to a more compact and rigid framework, MoO_3 increases structural complexity and disorder by introducing MoO_4 units and Mo-O-Mo linkages. These contrasting behaviors highlight the complementary roles of these modifiers in the adaptation of the structural and functional properties of TeO_2 -based glasses. The results align with the Raman spectroscopy findings, reinforcing the understanding of the structural dynamics induced by these oxides in the vitreous network.

4.1.5 Optical properties

Figure 23 presents the ultraviolet-visible (UV-Vis) absorption spectra for the studied samples, measured in the range of 300 to 850 nm. These spectra display the optical absorption coefficient as a function of wavelength. The absorption coefficient was calculated using the Beer-Lambert law, which describes light attenuation within a material and is expressed by the following equation (Davis; Mott, 1970):

$$I = I_0 e^{-\alpha L} \quad (4.2)$$

Figure 23 – Optical absorption spectra of the studied glasses: **(a)** Samples containing alkali metals (Li, Na, and Ba); **(b)** Samples containing molybdenum oxides, illustrating the variations in optical absorption properties due to compositional differences.



From the optical absorption data in the UV-Vis range, the band gap energy (E_g) can be determined. Using the method proposed by Davis and Mott (Davis; Mott, 1970), the type of electronic transition in a vitreous system is identified by relating the absorption coefficient (α) to the photon energy ($h\nu$). This relationship is expressed by the following equation.

$$\alpha(h\nu) \propto (h\nu - E_g)^m \quad (4.3)$$

Where α is the absorption coefficient, $h\nu$ represents the incident photon energy, and E_g is the band gap energy. The values of E_g are determined from Equation 4.3 by plotting $(\alpha E)^{(\frac{1}{m})}$ against E (where $h\nu = E$) in the absorption region. The band gap energy is obtained by extrapolating the linear portion of the plot to the point where $(\alpha E)^{(\frac{1}{m})} = 0$.

The type of electronic transition in the material is determined by the transition exponent, m , which characterizes the nature of electronic transitions. These transitions can be classified as direct allowed ($m = 1/2$), indirect allowed ($m = 2$), direct forbidden ($m = 3/2$), and indirect forbidden ($m = 3$). In this study, the direct allowed transition ($m = 1/2$) provided the best fit to the data. However, for completeness, the optical band gap values for both direct and indirect transitions are presented in Table 4 and Table 5, respectively, corresponding to $m = 1/2$ and $m = 2$ (Moraes et al., 2010). The behavior of direct transitions is illustrated in Figure 24, with additional figures and analyses provided in the appendix D.

Table 4 – Band gap values (E_g), oxide polarizability (η_0^{2-}), and optical basicity (Λ) for allowed direct electronic transitions.

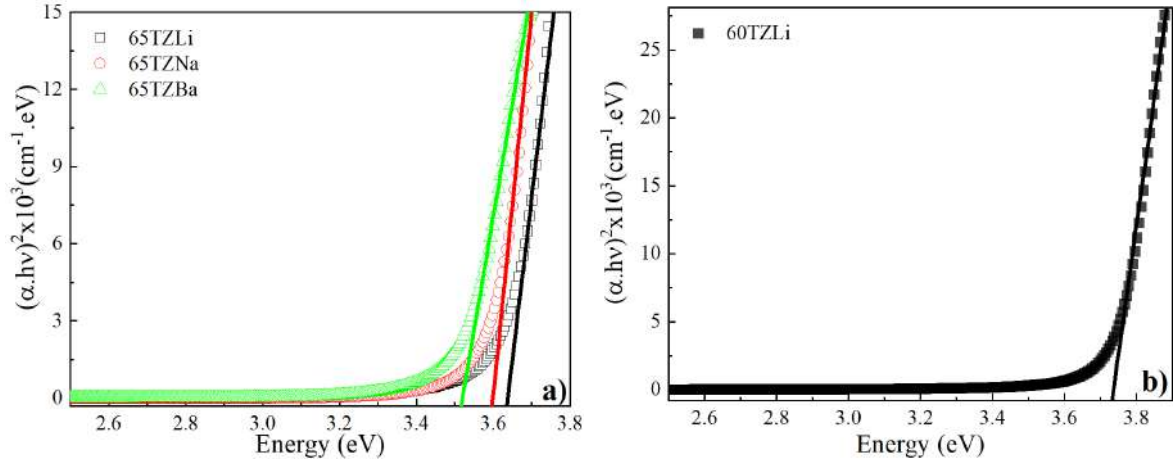
Sample	Direct $m = 1/2$		
	E_g (eV)	η_0^{2-} (E_g)	Λ
65TZLi	3.638 ± 0.015	2.751	1.063
65TZNa	3.569 ± 0.096	2.914	1.097
65TZMo	2.422 ± 0.030	2.984	1.110
65TZBa	3.520 ± 0.070	2.882	1.091
60TZLi	3.737 ± 0.019	2.763	1.065
60TZMo	2.598 ± 0.018	2.940	1.102

Table 5 – Band gap values (E_g), oxide polarizability (η_0^{2-}), and optical basicity (Λ) for allowed indirect electronic transitions.

Sample	Indirect $m = 2$		
	E_g (eV)	η_0^{2-} (E_g)	Λ
60TZNa	3.367 ± 0.038	3.046	1.122
60TZBa	3.309 ± 0.040	3.000	1.113

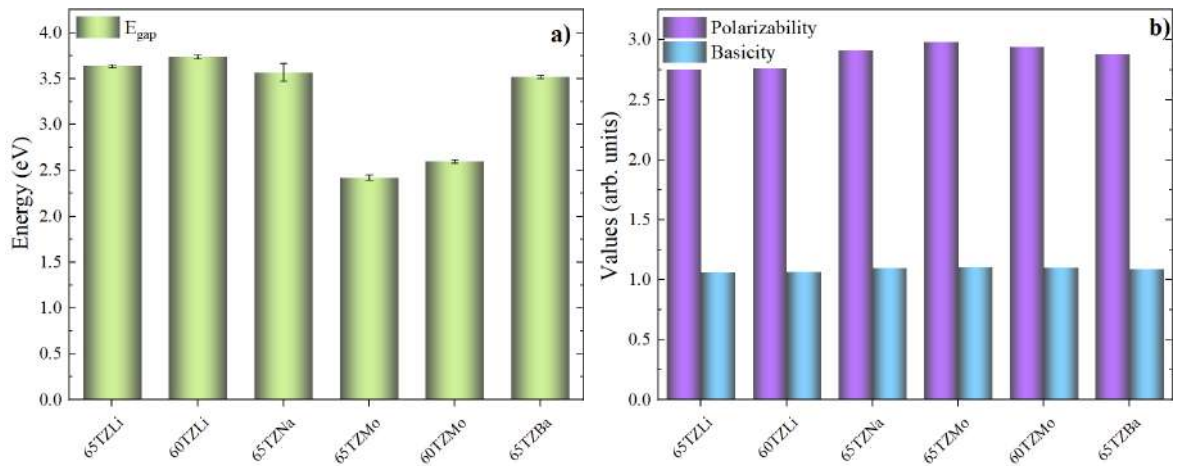
The introduction of alkali oxides, such as Li_2O and Na_2O , into tellurite glasses enhances optical transparency compared to other samples, as demonstrated in Figure 11. Figure 25 illustrates the behavior of the energy gap (E_g), the polarizability of oxide ions and the optical basicity for the allowed direct transitions, as discussed in Section 3.9. Samples containing Li_2O exhibit the highest E_g values (60TZLi: 3.737 eV and 65TZLi: 3.638 eV, Table 4), indicating that the addition of alkali oxides stabilizes the glass network by reducing structural disorder and influencing the distribution of electronic states within the band gap. Literature comparisons confirm these findings, with Na_2O -modified tellurite glasses exhibiting E_g values in the range of 3.3–3.5 eV, corroborating that the introduction of Na_2O and Li_2O effectively widens the energy gap (Fong et al., 2021; Jat et al., 2021).

Figure 24 – Plots of $(\alpha h\nu)^m$ versus photon energy for direct electronic transitions in alkali-containing groups: (a) Group 65; (b) Group 60.



This effect can be attributed to the ionic fields of these modifiers, which strengthen the glass network by reinforcing the bonds between oxygen atoms and cations, resulting in a more homogeneous material that is less prone to unwanted absorption near the ultra-violet edge. Moreover, the lower presence of non-bridging oxygens (NBOs) in Li_2O - and Na_2O -containing samples further enhances network stability and increases E_g . The reduction in NBOs strengthens the structural connectivity within the glass matrix, minimizing the likelihood of forming intermediate electronic states. Consequently, this combination of a stabilized glass network and reduced NBO content yields glasses with superior optical transparency and an increased energy gap.

Figure 25 – Graphical representation of the optical properties of the studied samples: (a) Band gap energy (E_g) for the direct allowed transition; (b) Oxide ion polarizability and optical basicity of the samples.



The 65TZBa and 60TZBa samples exhibit intermediate E_g values (3.255 eV for direct allowed transitions and 3.308 eV for indirect allowed transitions), consistent with previous findings on BaO-modified tellurite glasses (Alfryyan et al., 2023; Sayyed et al., 2023b). The high polarizability and optical basicity of BaO play a key role in stabilizing the glass network and promoting structural homogeneity, minimizing the formation

of dispersed electronic states within the allowed band and improving optical transition efficiency (Tasheva; Dimitrov, 2020). This polarizability, reflecting the deformability of oxygen ions under an electric field, reduces local lattice potential variations, resulting in a well-defined energy gap. Furthermore, the high optical basicity strengthens the cation-anion bonds within the glass, reducing the number of non-bridging oxygens (NBO) and yielding a more stable and defect-resistant network (Sayyed et al., 2023).

In contrast, the introduction of MoO_3 into tellurite glasses, as observed in the 65TZMo and 60TZMo samples, significantly reduces E_g values (2.183 eV and 2.324 eV, respectively). This reduction aligns with the ability of MoO_3 to introduce additional electronic states within the allowed band (Gomes et al., 2018). The formation of $[\text{MoO}_6]$ octahedra contributes to this effect, since their broad absorption band spanning the ultraviolet to blue-violet spectrum shifts the UV cut-off to longer wavelengths (Wang et al., 2017; Dutta; Khanna, 2012). The distortion of these octahedra elongates the Mo-O bonds, lowering the excitation energy required for charge transfer states (CTS) and further decreasing E_g .

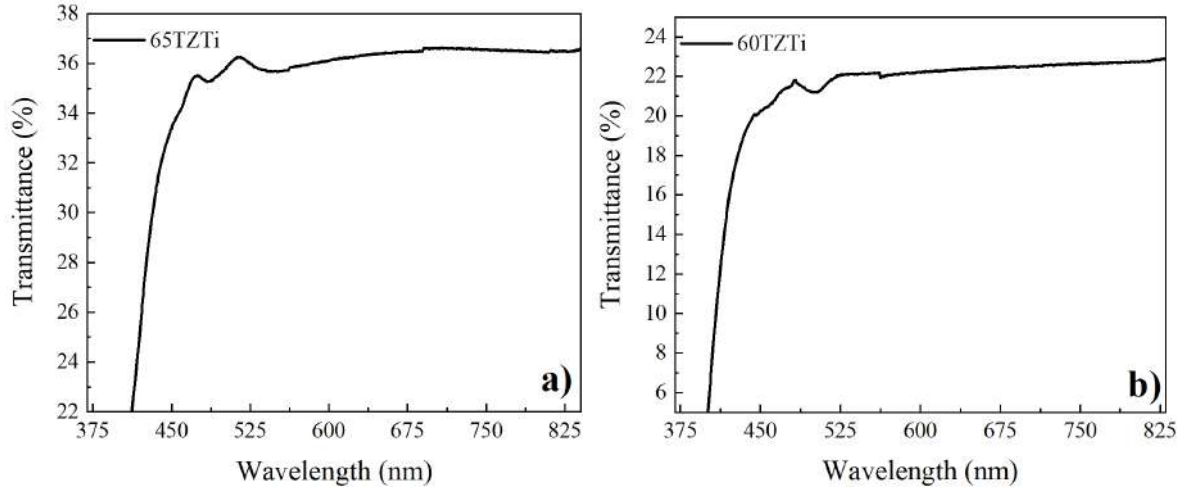
Raman results confirm that MoO_3 alters the glass network by promoting the substitution of Te-O-Te bonds with Te-O-Mo bonds, leading to an increase in NBOs. This structural reorganization introduces greater disorder while maintaining connectivity through MoO_4 and MoO_6 units, which are intercalated in the network. The observed increase in oxide ion polarizability (η_0^{2-}) in MoO_3 modified glasses supports these findings and aligns with the trends reported for glasses containing transition-metal oxides. These modifications underscore the dual role of MoO_3 as a network modifier and stabilizer, enhancing structural and optical properties while introducing a controlled level of disorder.

Figure 26 presents the results obtained for the 65TZTi and 60TZTi samples. The addition of TiO_2 to tellurite glasses, as observed in these samples, presents challenges in accurately determining their optical properties due to the coexistence of the oxidation states of Ti^{3+} and Ti^{4+} , indicated by absorption peaks at 473 nm and 513 nm. Studies show that these states are associated with distinct absorption bands: Ti^{3+} is particularly related to absorption in the red and near-infrared regions, while Ti^{3+} - Ti^{4+} complexes can induce charge transfer transitions, resulting in significant absorption within the visible spectrum (Bausa et al., 1991; Andrade et al., 2008).

The strong coloration of the samples suggests a predominant presence of Ti^{4+} , consistent with their preparation in an oxidizing atmosphere (air). The composition adjustment, with a 5% reduction in TeO_2 compensated by an increase in ZnO , further influences the structural and optical properties. This change improves the interaction between the ZnO and TiO_2 units, stabilizing the Ti^{4+} oxidation state and reducing the contribution of Ti^{3+} . Consequently, the UV cutoff is redshifted as a result of the increased polarizability of the glass network, while the complexity of the optical characterization process highlights the need for advanced techniques to fully resolve the interplay between

structural modifications and electronic transitions.

Figure 26 – Optical transmittance spectrum in the wavelength range of 375 to 825 nm for samples with a thickness of 300 μm . (a) Sample 65TZTi. (b) Sample 60TZTi.



4.2 VICKERS HARDNESS

The Vickers hardness values H_V of the prepared glasses were determined using Equation 3.5, which is based on the deformation and fracture patterns observed during Vickers indentation tests. Investigating Vickers hardness across various glass compositions offers valuable insights into how the incorporation of different modifying oxides enhances the mechanical strength of these materials. Figure 27 (a) presents the Vickers hardness values for the 65TZ group, while Figure 27 (b) depicts the values for the 60TZ group, tested under applied loads of 3 N and 5 N.

Figure 27 – (a) Vickers hardness values for the 65TZ group. (b) Vickers hardness values for the 60TZ group. Both measured under applied loads of 3 N and 5 N.

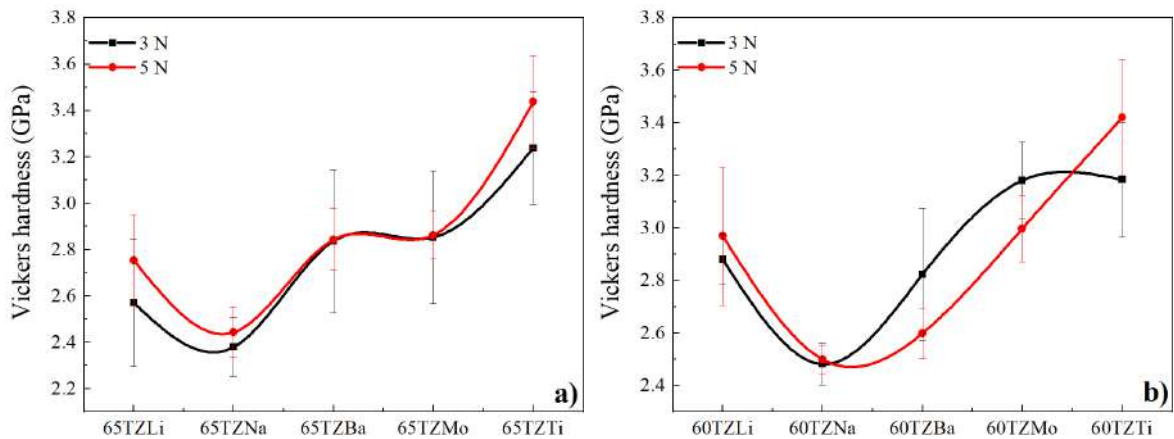
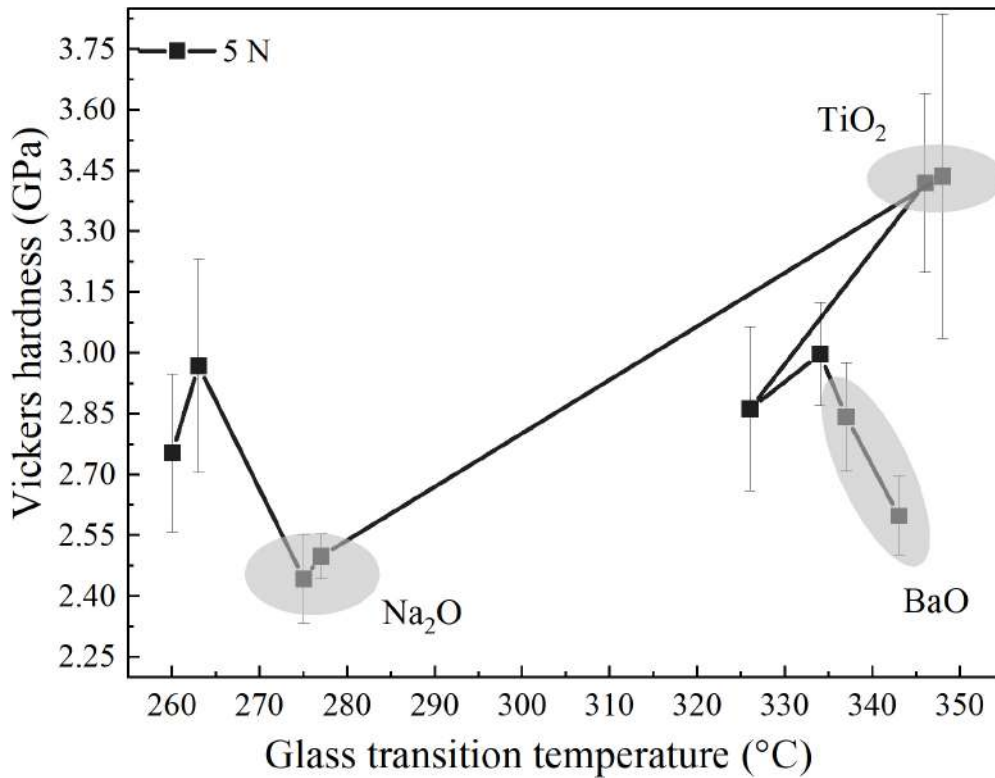


Figure 28 illustrates the correlation between Vickers hardness and glass transition temperature (T_g) for glasses containing different oxides. The trailing Vickers hardness

against T_g is particularly insightful because T_g serves as a fundamental indicator of the structural rigidity and thermal stability of the glass network. A higher T_g typically reflects stronger chemical bonding and a more connected glass structure, which is directly correlated with increased mechanical strength, including hardness.

In particular, the highest values of both Vickers hardness and T_g are observed in samples containing TiO_2 , which is attributed to its ability to enhance the structural connectivity of the glass network. Samples containing BaO exhibit intermediate values, reflecting the role of BaO as a network modifier that increases density while partially stabilizing the network. In contrast, glasses containing Na_2O show the lowest values of both Vickers hardness and T_g , consistent with the disruptive effect of Na_2O on the glass network, which reduces the overall rigidity and cohesion.

Figure 28 – Relationship between Vickers hardness and glass transition temperature (T_g) of the prepared glasses. The line serves as a visual guide.

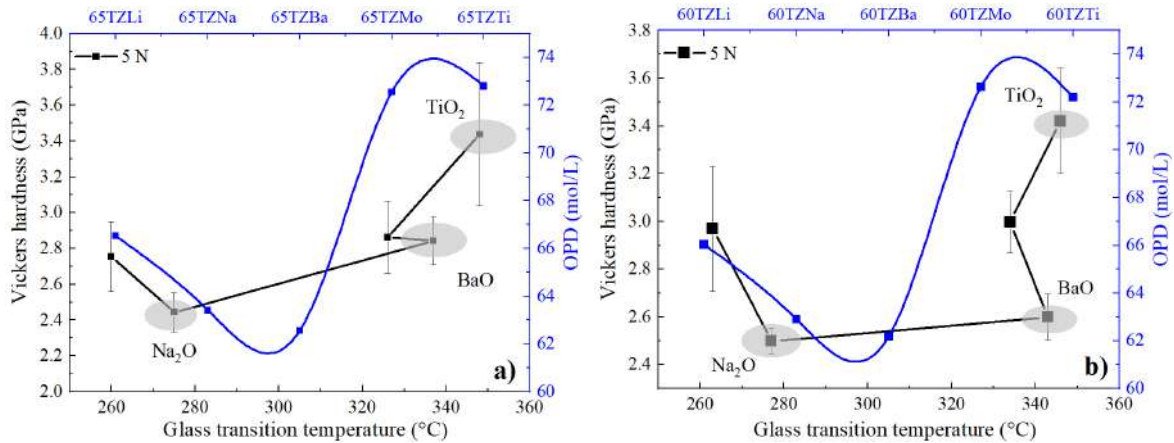


A clear linear relationship is evident between the TiO_2 content and the increase in both the Vickers hardness and T_g of the glasses. Vickers hardness values reach up to approximately 3.43 GPa, while T_g approaches 345 °C for glasses with a high TiO_2 content, such as samples 60TZTi and 65TZTi. These results demonstrate that TiO_2 acts as an effective network former, significantly increasing the packing density within the glass structure. The rigid network, characterized by a large number of strong Ti-O bonds, provides a cohesive and deformation-resistant structure, which explains the observed higher hardness and T_g . This synergy between high hardness and T_g makes TiO_2 -based glasses particularly promising for applications that require both durability and thermal stability.

These findings align with similar trends reported in the literature, which highlight improvements in mechanical and thermal properties, including hardness, for systems such as 15K₂O–15Nb₂O₅–70TeO₂ and 70TeO₂–15ZnO–15Na₂O, among others (Torres et al., 2001; Watanabe et al., 1999; Sidkey et al., 1997).

The blue line in Figures 29 (a) and 29 (b) represents the oxygen packing density (OPD), a parameter indicative of the structural compactness of the glass network. Higher OPD values correspond to a denser and more efficiently packed structure, which strongly influences the mechanical and thermal properties of glasses. For samples containing TiO₂, the OPD values reach their maximum, aligning with the highest Vickers hardness and T_g values. This relationship indicates that the incorporation of TiO₂ significantly enhances the packing efficiency within the glass network by increasing the number of strong Ti–O bonds. These bonds contribute to a more cohesive structure, reducing free volume and improving the network capacity to resist deformation under load. The strong correlation between OPD and mechanical properties suggests that TiO₂ acts as an effective network former, driving improvements in both hardness and thermal stability.

Figure 29 – (a) Relationship between Vickers hardness and glass transition temperature (T_g) for the 65TZ series under a 5 N load. The blue line represents the Oxygen packing density (OPD), highlighting the structural compactness. TiO₂-modified glasses exhibit the highest OPD, hardness, and T_g , while Na₂O-modified samples show the lowest. (b) Similar trends are observed for the 60TZ series, emphasizing the role of TiO₂ as a network former and Na₂O as a network modifier.



In contrast, Na₂O-modified samples, particularly 60TZNa and 65TZNa, exhibit the lowest Vickers hardness (~ 2.44 GPa) and T_g (~ 275 °C) values. Acting as a network modifier, Na₂O introduces non-bridge oxygens into the glass structure, resulting in less cohesive structural units and an open and less compact matrix. This structural disruption reduces both the mechanical strength and thermal stability, making these glasses more prone to deformation under load. The low OPD values of Na₂O-modified glasses further highlight the detrimental effect of this modifier, as the reduced packing density correlates with the observed lower hardness and T_g . The low T_g also indicates reduced resistance to thermal softening, limiting their application in high-temperature environments (Yousef et al., 2012).

Interestingly, BaO-modified samples show intermediate OPD values, reflecting the dual role of BaO as both a density enhancer and a network stabilizer. Although BaO increases the overall packing density compared to Na₂O, it does not achieve the same level of structural compactness as TiO₂, resulting in moderate mechanical and thermal properties. This dual behavior is evident in the intermediate values of Vickers hardness and T_g for samples containing BaO.

The response of glasses under different test loads (3 N and 5 N) reveals a trend in which Vickers hardness increases with applied load. This behavior is attributed to the further compaction of the glass network under higher loads, making it more difficult for the indenter to penetrate. In particular, samples containing TiO₂ consistently exhibit the highest hardness under all loads, peaking at up to 4.0 GPa under a 5 N load. This trend confirms that the TiO₂-modified glass matrix maintains its structural integrity even under significant loads, reflecting excellent mechanical strength (Kabalci et al., 2017; Oliveira Lima et al., 2022).

In contrast, samples containing Na₂O show greater variability in hardness values as the load increases, particularly under lower loads. This variability reflects reduced mechanical strength and greater sensitivity of the network to small deformations, which may pose limitations in applications where glasses experience variable forces or repeated impacts. To further support the Vickers hardness results, optical microscopy analyses were conducted. Additional findings that enrich the discussion presented in this chapter can be found in the appendix D.

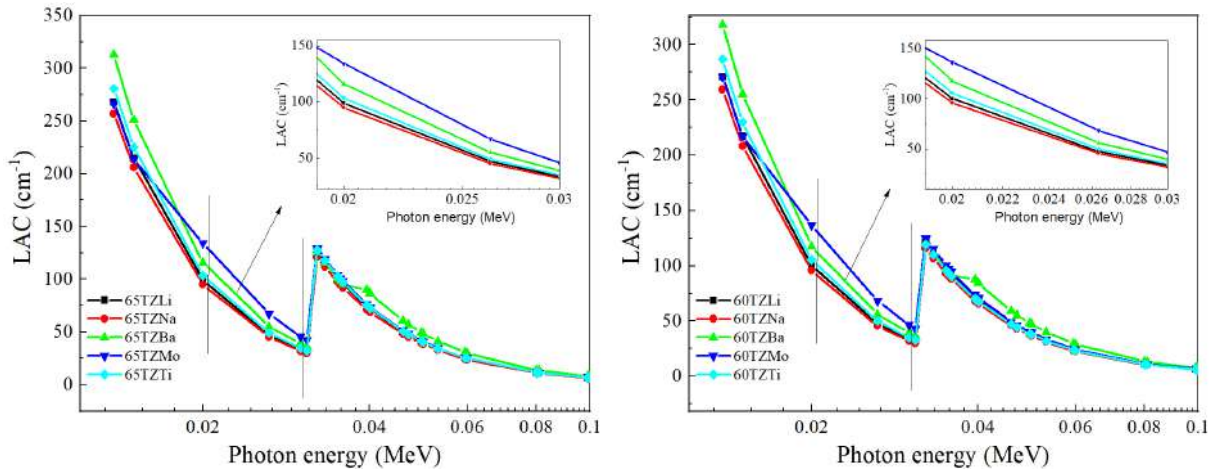
4.3 RADIATION PROPERTIES

4.3.1 Linear Attenuation Coefficients

The theoretical linear attenuation coefficients (LAC) of the prepared glass samples, simulated using Phy-X/PSD (Şakar et al., 2020), are presented over an energy range of 0.01 to 100 keV in Figure 30. Understanding LAC is crucial for applications in radiation shielding and medical imaging, as it determines a material capacity to attenuate radiation at various energy levels. The data reveal that samples containing BaO exhibit superior attenuation performance, particularly at lower energy levels. For example, at the lowest evaluated energy, the LAC values for the TZBa samples are 313 cm⁻¹ (65TZBa) and 318 cm⁻¹ (60TZBa), significantly higher than those for TZNa samples, which display LAC values of 256 cm⁻¹ and 259 cm⁻¹, respectively.

However, a closer examination of specific energy regions indicates that the enhanced performance of TZBa samples is not consistent across all energy levels. This variation suggests that, while BaO enhances attenuation properties in certain energy ranges,

Figure 30 – Linear Attenuation Coefficient (LAC) of 60TZ and 65TZ glass samples as a function of photon energy (0.01 to 0.1 MeV). The inset focuses on LAC variations at low energies (0.02 to 0.03 MeV), demonstrating that BaO-doped glasses (65TZBa and 60TZBa) exhibit the highest attenuation efficiency in this range.



other compositional factors, such as oxide concentration and glass network connectivity, also influence performance. In the energy range highlighted in the inset of Figure 30 (between 20 and 30 keV), the highest attenuation is observed in the TZMo samples ². For example, the superior performance of TZMo in the 20–30 keV range is due to the predominance of the photoelectric effect, which is highly dependent on the atomic number and electronic configuration of the modifying elements. Furthermore, the presence of MoO₃, in combination with other oxides, has been shown to enhance gamma radiation resistance, which is critical for applications in high-radiation environments (Liu et al., 2019).

Alzahrani et al. demonstrated that in the TeO₂-Na₂O-TiO₂ glass system, the LAC is higher at low energies (0.015 keV), dominated by the photoelectric effect, and decreases with increasing energy due to Compton scattering and pair production (Alzahrani et al., 2021). M.S. Al-Buriah et al. evaluated systems such as BaO-TeO₂-WO₃, BaO-TeO₂-Y₂O₃, BaO-TeO₂-Sr, and BaO-TeO₂-Li₂O, showing that LAC values decrease with increasing photon energy, primarily due to the photoelectric effect. These results highlight the influence of the absorption edges and component density on the radiation absorption capacity (Alonizan et al., 2023). In addition, molybdenum presents a K-edge energy at 19.9 keV, which, although not evident in the graph due to the overlap with the K absorption of tellurium, contributes significantly to better attenuation in this region, surpassing the sample with BaO, which has a higher overall LAC, but not in the 20-30 keV energy region.

At the K-edge absorption energy of tellurium (32 keV), the difference in attenuation

² This can be attributed to the different types of interactions that dominate at specific energy levels: the photoelectric effect at lower energies, Compton scattering at intermediate energies, and pair production at higher energies. Further details on the photoelectric effect, Compton scattering, and pair production can be found in the appendix B.

effectiveness between the 65TZ and 60TZ glass families becomes more pronounced, leading to distinct variations for samples containing different modifying elements. The higher attenuation values observed for the 65TZ samples are directly related to their increased concentration of Te, which significantly enhances photon absorption at the K-edge, a crucial factor for radiation shielding in this energy range.

Sayyed et al. noted that in the BaO-MoO₃-B₂O₃-TeO₂ system, the LAC of the glasses increases with higher TeO concentration and decreases with increasing photon energy. This occurs because high-energy photons interact less with the material. The steep decline in LAC at lower energies is primarily due to photoelectric absorption, while Compton scattering dominates at higher energies. The MTB5 glass (70 mol% TeO₂) outperformed other tellurite glasses (Al-Ghamdi et al., 2021; Teresa et al., 2021; Kaky et al., 2020) in terms of radiation attenuation, highlighting the significance of high TeO₂ content in enhancing shielding properties compared to existing boro-tellurite glasses (Sayyed et al., 2022; Divina et al., 2020).

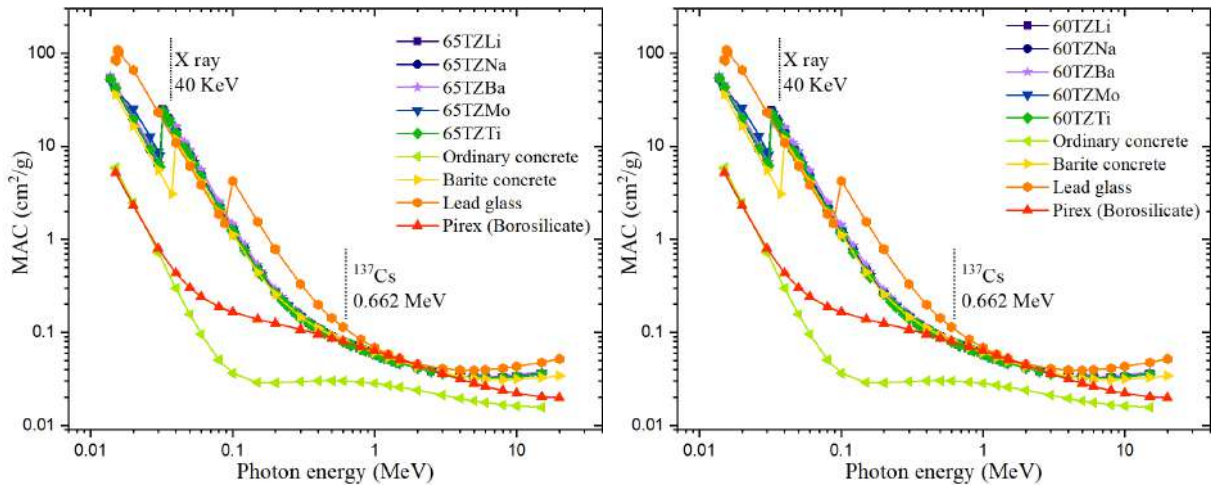
Although the LAC provides information on how much radiation is attenuated per unit thickness, it is directly influenced by the density of the material, making it difficult to compare glasses of varying densities. However, a parameter called Coefficients (MAC) normalizes this effect by accounting for the mass of the material, allowing for a more accurate comparison of the inherent shielding properties of different glasses. This ensures that the effectiveness of the material is evaluated on the basis of its atomic composition and interaction with radiation, rather than just its thickness or density, leading to more informed decisions in selecting appropriate shielding materials.

4.3.2 Mass Attenuation Coefficients

Figure 31 presents the theoretical mass attenuation coefficients (MAC) of the prepared glass samples up to 15 MeV, compared to some conventional shielding materials, including ordinary concrete, barite concrete, lead glass and Pyrex (borosilicate). The data illustrate how attenuation behavior varies across different energy levels, mainly influenced by the specific composition of the glass samples.

In particular, the 65TZ family of samples (Figure 31 -a) consistently shows slightly higher MAC values compared to the 60TZ series (Figure 31-b). For example, for the sample enriched with BaO, at the highlighted energy of 40 keV in the figure, the values are 16.05 and 15.68 cm²/g for the 65TZBaO and 60TZBa samples, respectively. This trend can be attributed to the higher concentration of tellurium (Te) in the 65TZ samples, which improves photon interaction probabilities. Sample 65TZLi contains 0.245 mol% of Te, while its counterpart, sample 60TZLi, has only 0.232 mol% of Te. Furthermore, the molar fraction of zinc (Zn) increases from 0.0714 to 0.0909 mol% in 65TZ samples, further

Figure 31 – Theoretical mass attenuation coefficients (MAC) of the prepared glass samples up to 15 MeV, compared with conventional shielding materials. (a) 65TZ glass series, (b) 60TZ glass series.



influencing their attenuation properties.

Compared with conventional shielding materials, both the 65TZ and 60TZ glass samples exhibit competitive attenuation characteristics, particularly at lower photon energies (below 0.1 MeV), where their MAC values are comparable to those of barite concrete and lead glass. As the photon energy increases, the MAC values of all materials, including the glass samples, decrease, following the expected trend because of the reduced probability of photon interaction at higher energies. However, samples from the 65TZ series, especially those containing barium (65TZBa), maintain relatively higher MAC values compared to Pyrex and ordinary concrete, indicating their superior effectiveness in high-energy shielding applications (Al-Qous, 2021).

Compared with studies in the literature, Rammah et al. analyzed the 80TeO₂-10BaO-Li₂O system over the energy range of 0.015 to 15 MeV. The results indicated that the MAC exhibited maximum values at low energies due to the dominance of photoelectric absorption, followed by a sharp decline up to 1 MeV, and smaller variations at higher energies where Compton scattering and pair production mechanisms prevail. A characteristic peak with a significant increase in MAC is also observed around 0.03181 MeV, attributed to the K-absorption edge of Te. The sample showed MAC values ranging from 41.048 cm²/g to 0.038 cm²/g across the evaluated energy spectrum (Rammah et al., 2020a).

Mhareb et al. evaluated the substitution of B₂O₃ with TeO₂ in the 20BaO-MoO₃-(70-x)B₂O₃:xTeO₂ system, which increases the MAC of the glasses due to the higher atomic number of Te (52) compared to B (5). At 15 keV, the MAC increases from 22.39 cm²/g to 42.15 cm²/g when the TeO₂ content increases to 70 mol%. At higher energies, the increase in MAC is slower, varying from 0.028 cm²/g to 0.035 cm²/g (20BaO-10MoO₃-70B₂O₃ to 20BaO-10MoO₃-70TeO₂) at 10 MeV, and from 0.028 cm²/g to 0.038 cm²/g at 15 MeV. These results indicate that increasing the TeO₂ content is an effective strategy

to enhance the attenuation capacity of glasses (Mhareb et al., 2021).

These results underscore the critical role of glass composition, particularly the concentration of high atomic number elements such as Te and Ba, in optimizing radiation attenuation properties. The higher concentrations of these elements in the 65TZ series contribute to more effective attenuation, especially at lower to intermediate photon energies. Consequently, these glasses offer a promising alternative to conventional shielding materials, offering advantages such as reduced weight and greater transparency while maintaining effective radiation protection capabilities.

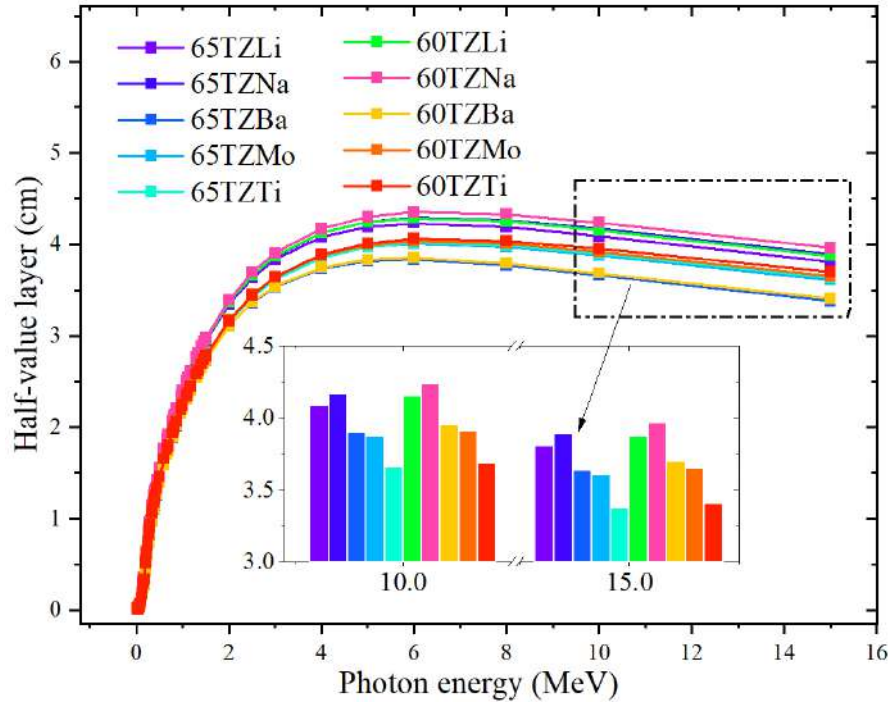
4.3.3 Half-Value Layer

The half-value layer (HVL) is a critical metric to assess the radiation shielding efficiency of materials, defining the thickness required to halve the intensity of incoming radiation. In this study, HVL values for glass samples from the 60TZ and 65TZ series, each modified with different oxides (Li, Na, Ti, Mo, Ba), were analyzed over a photon energy range of 0 to 14 MeV. The results, displayed in Figure 32, reveal varied attenuation behaviors across different energy regions. Mhareb et al. compared the HVL of current glasses with that of other glasses to evaluate their radiation attenuation performance. It is evident that the HVL of the boro-tellurite glass system $20\text{BaO-MoO}_3-(70-x)\text{B}_2\text{O}_3:x\text{TeO}_2$ is lower than that of RS 253 G18, while the HVL of BTM4 ($20\text{BaO-10MoO}_3-17.5\text{B}_2\text{O}_3-52.5\text{TeO}_2$) is close to that of RS 360, attributed to its higher TeO_2 concentration (Kaur et al., 2019; Mhareb et al., 2021).

At low photon energies (0 to 4 MeV), the HVL values increase rapidly with increasing energy, suggesting that thicker glass layers are needed to attenuate low-energy photons effectively. This is primarily due to the dominance of the photoelectric effect in this range, which leads to higher photon-matter interaction cross-sections. Among the different samples, those doped with BaO (65TZBa and 60TZBa) exhibit the lowest HVL values, indicating superior attenuation capabilities. This performance can be attributed to the high atomic number of barium, which enhances photoelectric absorption, making these glasses particularly effective in this energy range. Y.S. Rammah et al. found that the HVL in the TTZF glasses is significantly influenced by density, with the $80\text{TeO}_2-4\text{Ta}_2\text{O}_5-4\text{ZnO-12ZnF}_2$ composition (density of 5.986 g/cm^3) exhibiting the lowest HVL values. The maximum HVL observed was around 3.5 cm, highlighting the effectiveness of glass for gamma-ray shielding. The observed variations in HVL are attributed to photon-matter interactions and secondary scattering, which contribute to the increased glass thickness required for effective shielding (Rammah et al., 2020c).

In the intermediate energy range (4 to 10 MeV), the HVL values for all samples stabilize or show a moderate increase. This shift reflects the transition from the photoelec-

Figure 32 – Half-Value Layer (HVL) of the prepared glass samples (60TZ and 65TZ series) as a function of photon energy (0 to 14 MeV). The inset focuses on HVL variations at 10 and 15 MeV, revealing that BaO-doped samples (65TZBa and 60TZBa) consistently exhibit lower HVL values, which suggests enhanced attenuation capabilities, particularly at lower photon energies.



tric effect to Compton scattering as the main photon interaction mechanism, which is less influenced by the atomic number. As indicated in the inset of Figure 32, glasses containing Na and Ti (60TZNa, 65TZNa, 60TZTi, 65TZTi) show slightly higher HVL values compared to those containing Ba, suggesting that these glasses may require a thicker layer to achieve comparable attenuation. The $\text{TeO}_2\text{-ZnO-Na}_2\text{O}$ system, investigated by M.S. Al-Buriah et al., demonstrates that substituting ZnO with Na_2O significantly impacts the radiation attenuation properties of the glass. Moreover, this composition showed the lowest HVL, indicating superior shielding performance, and the lowest MFP, reflecting enhanced photon interaction (Al-Buriah et al., 2022).

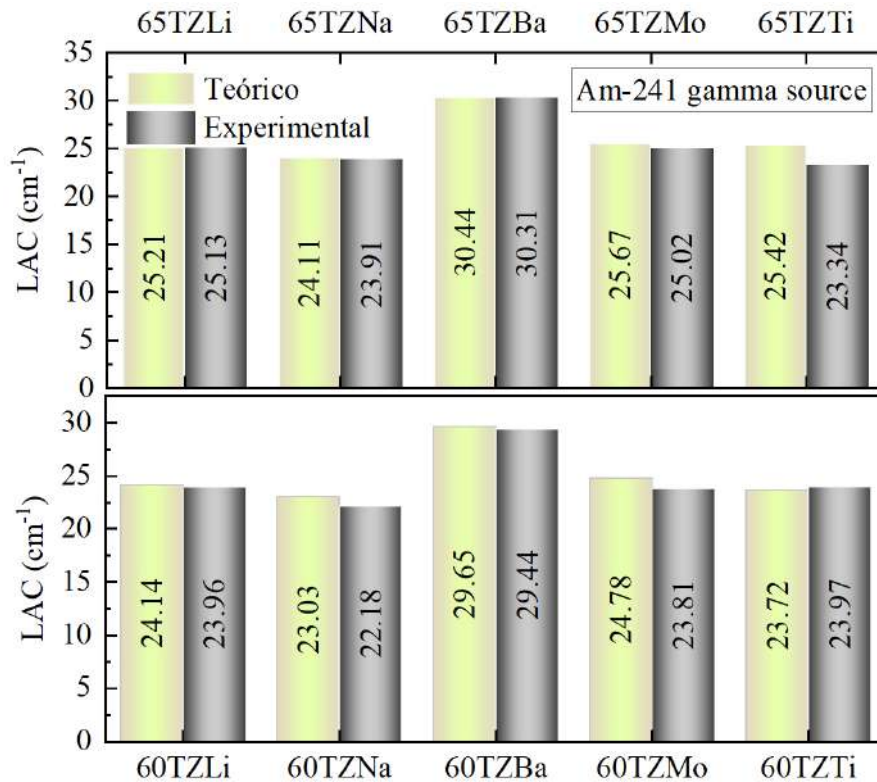
At higher photon energies (10 to 14 MeV), the HVL values for all samples tend to converge, indicating reduced differences in attenuation efficiency across the different compositions. This trend is due to the increasing significance of pair production at these energies, which is a process less dependent on the atomic composition of the materials. Despite this convergence, BaO-containing glasses (65TZBa and 60TZBa) continue to maintain slightly lower HVL values, highlighting their broad-spectrum effectiveness in radiation shielding applications.

4.3.4 Attenuation For Specific Radioisotopes - Experimental measurements

To evaluate the factual radiation attenuation effectiveness of the prepared glass samples at specific energy levels, particularly those emitted by americium-241 (Am-241) and cobalt-57 (Co-57) radioisotopes, experimental measurements were performed, as described in section 3.12. The results, presented in Figures 33 and 34, were compared with theoretically predicted values to assess both the accuracy of the simulations and the practical performance of these materials.

Figure 33 illustrates the experimental and theoretical LAC for the Americium-241 (Am-241) radioisotope. The data show that the 65TZ glass family generally exhibits slightly higher theoretical LAC values than the 60TZ series across all samples. This difference is primarily due to the increase in tellurium (Te) concentration in the 65TZ samples. For example, sample 65TZLi contains 0.245 mol% of Te, compared to 0.232 mol% in sample 60TZLi. Furthermore, the molar fraction of zinc (Zn) is higher in the 65TZ series (0.0909) than in the 60TZ series (0.0714), further contributing to the enhanced attenuation properties.

Figure 33 – Experimental and theoretical mass attenuation coefficients (LAC) of the prepared glass samples for Americium-241 (Am-241) radioisotope. The comparison highlights the differences between experimental measurements and theoretical predictions, showing that TZBA samples (65TZBa and 60TZBa) consistently exhibit higher attenuation capabilities.



Regarding modifying oxides, all samples demonstrated stable attenuation characteristics close to 25 cm⁻¹, except for TZBa glasses, which stood out with an LAC of

approximately 30 cm^{-1} . This suggests that the presence of BaO enhances the attenuation capability, likely because of the high atomic number of barium, which increases the probability of photoelectric interactions.

Although the theoretical and experimental results were closely aligned, it is essential to emphasize the importance of experimental measurements for accurate assessments, particularly when dealing with potentially hazardous radiation. In particular, the experimental LAC values were consistently lower than the theoretical predictions. This discrepancy could result from various factors related to the sample preparation process, such as material volatilization or uneven distribution of the molten liquid in the crucible, leading to microstructural discontinuities. Thus, experimental data provide a more realistic evaluation of the effectiveness of materials in practical radiation shielding scenarios.

Figure 34 presents the experimental and theoretical LAC for the Cobalt-57 (Co-57) radioisotope. As expected, the attenuation values for Co-57 were significantly lower than those for Am-241, directly reflecting the higher energy of Co-57 photons. Similarly to the results for americium, the 65TZ glass family showed more effective attenuation, which can be attributed to the higher concentration of tellurium oxide. Again, the experimental values were slightly lower than the theoretical predictions, but remained in close agreement, validating the overall accuracy of the theoretical models. These observations highlight the effectiveness of the 65TZ glass series, particularly those with BaO composition, in attenuating the radiation emitted by Am-241 and Co-57, demonstrating their superior absorption capacity across different energy ranges.

4.3.5 Radiation Protection Efficiency

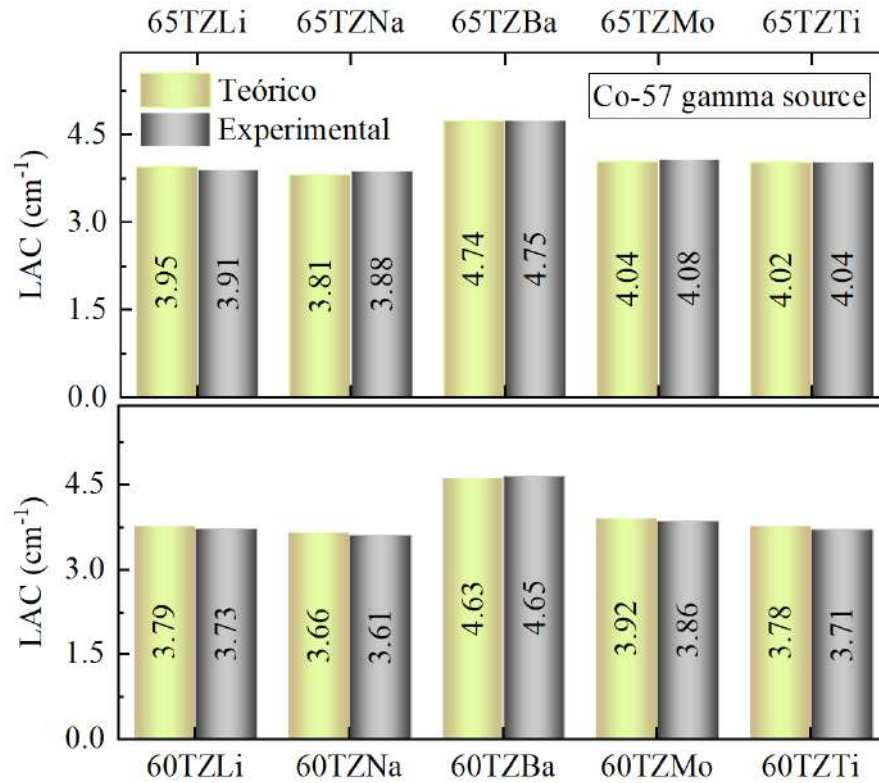
Radiation Protection Efficiency (RPE) is a vital measure for assessing the capacity of glass materials to protect against ionizing radiation. It is mathematically expressed by the following equation:

$$RPE = (1 - e^{-\mu x}) \quad (4.4)$$

where x represents the thickness of the glass sample and μ is the linear attenuation coefficient. This formula provides a way to quantify the level of radiation protection a material can offer at a given thickness. To evaluate the potential of thin glass layers for radiation shielding—an attractive proposition due to their lightweight nature and optical transparency. Figure 35 presents the RPE values for glass samples with thicknesses of 1 mm and 5 mm, based on experimental measurements using Americium-241 (Am-241) and Cobalt-57 (Co-57) radioisotopes.

The experimental results reveal that glass samples are highly effective in attenuating radiation even at minimal thicknesses. For example, a sample of 1 mm thick achieves

Figure 34 – Experimental and theoretical mass attenuation coefficients (LAC) of the prepared glass samples for the Cobalt-57 (Co-57) radioisotope, illustrating the attenuation properties of different glass compositions and their alignment with theoretical predictions.

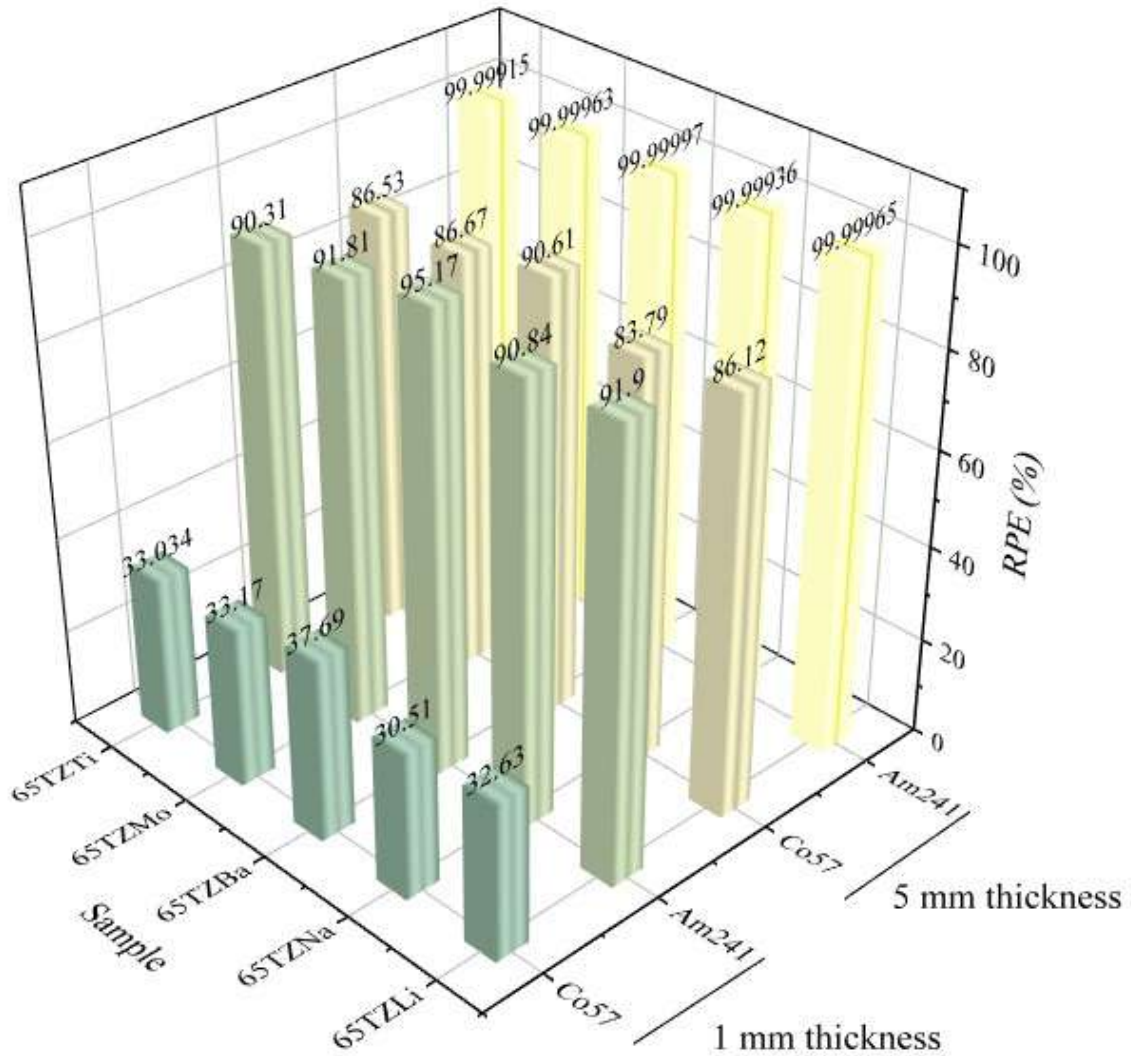


attenuation efficiencies ranging from 32% to 38% for Co-57, while for Am-241, the same thickness results in efficiencies between 92% and 95%. This difference is due to the lower photon energy associated with Am-241, which is more readily absorbed by glass materials.

Kozlovskiy et al. reported that the $\text{TeO}_2-(1-x)\text{ZnO}-x\text{Sm}_2\text{O}_3$ glass system with 10 mm thickness can block up to 75% of radiation at 136 keV and between 55% and 70% at 661 keV, with $\text{TeO}_2-0.2\text{ZnO}-0.8\text{Sm}_2\text{O}_3$ being the most effective, absorbing 55% to 80% of radiation. This efficiency is attributed to the increase in the absorption coefficients and the formation of electron traps. However, the absence of ZnO reduces the shielding efficiency, indicating that ZnO also contributes to radiation absorption, influencing the structural properties of glasses (Kozlovskiy et al., 2021).

This evidence suggests that relatively thin layers of glass can offer substantial radiation protection, particularly against low-energy photons. For example, a glass layer of 7 mm thick is sufficient to achieve nearly complete attenuation (100%) of Am-241 radiation for most samples, except for 65TZNa and 65TZTi, which require an 8 mm thick layer to ensure complete protection. In contrast, for Co-57 radiation, which involves higher energy photons, a significantly higher thickness of at least 50 mm is required for full attenuation, while a thickness of 40 mm is adequate for samples containing barium (Ba), owing to its enhanced attenuation capabilities.

Figure 35 – Presents the theoretical radiation protection efficiency (RPE) of the 65TZx glass samples at thicknesses of 1 mm and 5 mm for Americium-241 (Am-241) and Cobalt-57 (Co-57) radioisotopes. The graph illustrates how varying thicknesses affect the glass samples ability to attenuate radiation from different radioisotopes, highlighting the effectiveness of the materials in providing shielding at specific thicknesses.

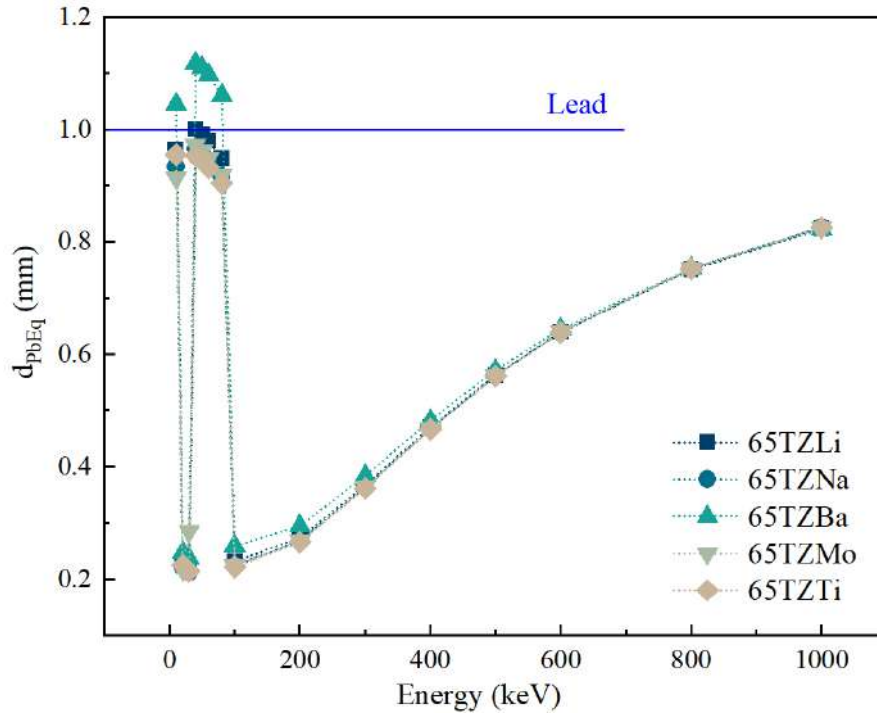


4.3.6 Lead Equivalent Thickness

The lead equivalent thickness (dPbEq) is a measure used to compare the radiation attenuation properties of different materials with that of lead, providing an equivalent thickness of lead that would offer the same level of radiation shielding (Karim et al., 2024). To assess the attenuation performance of the 65TZ glass samples, the equivalent lead thickness corresponding to 1 mm of pure lead was calculated in a photon energy range of 10 to 1000 keV, as shown in Figure 36.

The results show that for photon energies below 100 keV, the prepared glass samples display shielding capabilities that are comparable to pure lead, with BaO-doped glasses achieving the highest performance, reaching a maximum lead equivalence of 1.12

Figure 36 – Lead equivalent thickness (dPbEq) of the glass samples at 1 mm thickness as a function of photon energy, illustrating their attenuation capabilities in comparison to that of pure lead.



mm at 40 keV. However, for photon energies exceeding 100 keV, there is a noticeable decline in shielding efficiency, where the equivalent lead thickness is reduced to approximately 0.25 mm. This decrease in effectiveness stabilizes at higher energy levels, eventually increasing to 0.8-mm lead equivalence at 1 MeV.

According to established standards, protective shields are required to achieve a specific lead equivalence greater than 0.22 mmPb/mm in the diagnostic medical X-ray energy range of 0.03–0.08 MeV (Wu et al., 2023; Zhao et al., 2024). For reference, the B_2O_3 - MnO_2 - CdO glass system has specific PbE values ranging from 0.241 to 0.294 mmPb/mm (Wu et al., 2023), while the B_2O_3 - TeO_2 - BaO - MO ($M = Bi, W, Cd, Mo$) achieves PbE values between 0.328 and 0.441 mmPb/mm. The glass samples prepared in this study exhibit average specific PbEq values approaching 1 mmPb/mm, indicating superior shielding effectiveness within the specified energy range.

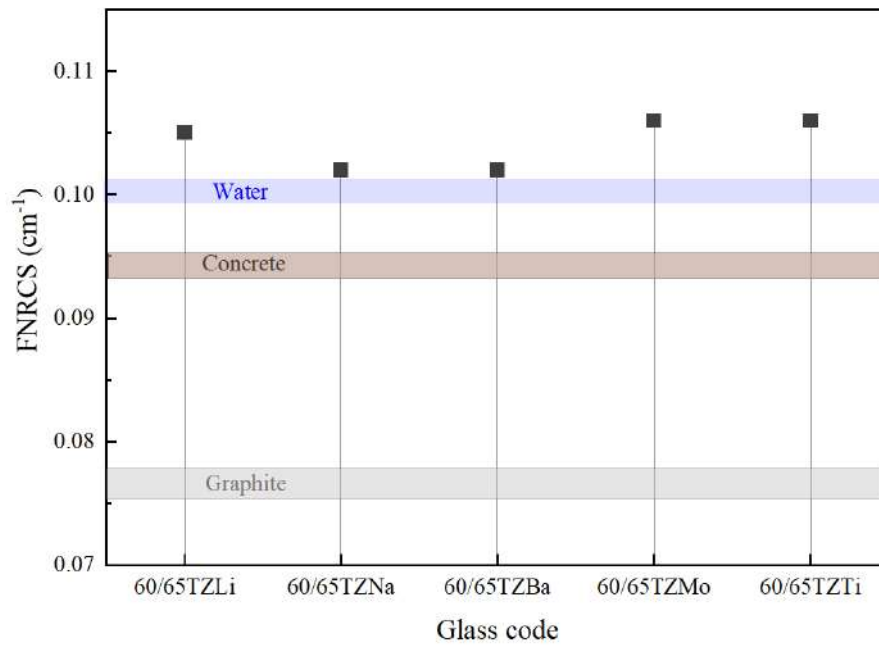
Throughout the entire energy range, the lead equivalence values of the prepared glasses consistently exceed the standard requirement of 0.22 mmPb/mm, highlighting their effectiveness as radiation shielding materials across a variety of applications.

4.3.7 Neutron Shielding Capabilities

The primary objective of this study is to enhance photon attenuation across a wide energy range using the developed materials, but it is also valuable to consider their po-

tential for neutron shielding. The macroscopic effective fast neutron removal cross-section (FNRCs or ΣR), serves as a critical metric in this regard. This parameter quantifies the likelihood that a fast or fission-energy neutron will experience an initial collision and be removed from the flux of penetrating, uncollided neutrons. This measure is particularly pertinent for fast neutrons within the energy range of 2 to 12 MeV, where the removal cross-section is typically considered relatively constant (El-Khayatt, 2010). The FNRCs values for the prepared glass samples are presented in Figure 37.

Figure 37 – shows the fast neutron removal cross-section (FNRCs) for the prepared glass samples. For comparative purposes, FNRCs values for conventional neutron shielding materials are also included, providing a broader context for evaluating the neutron shielding capabilities of the studied glass samples.



All prepared samples exhibited values greater than 0.10 cm⁻¹, and, as shown in Figure 37, higher than reference materials such as graphite, concrete and water. El-Khayatt (El-Khayatt, 2010) has observed that the cross-section of mass removal of compounds is primarily determined by the mass fraction of their lighter constituent elements rather than their molar masses. Although lighter elements generally exhibit higher mass removal cross-sections, this trend does not uniformly apply to all compounds. The data indicates that other factors, such as the composition and spatial distribution of elements within the compound, play a significant role in determining the removal cross-section. This explains why water (H₂O), despite its low molar mass, possesses a high neutron shielding capability; the effectiveness of water in blocking neutrons is largely due to its substantial mass fraction of hydrogen, which significantly contributes to its high mass removal cross-section. Neutrons primarily lose energy through collisions with light atoms, particularly hydrogen, due to their comparable mass. In water, fast neutrons transfer a substantial portion of their energy when colliding with hydrogen nuclei. After multiple such interactions, neutrons slow down to thermal energies through a process known as

neutron moderation.

Ersundu et al. observed that $\text{WO}_3\text{-MoO}_3\text{-TeO}_2$ glasses exhibit higher fast neutron removal cross sections compared to standard shielding concrete. The $10\text{WO}_3\text{-20MoO}_3\text{-70TeO}_2$ and $10\text{WO}_3\text{-10MoO}_3\text{-80TeO}_2$ (heavy metal oxide glasses) were found to be nearly as effective as lead glass in fast neutron shielding, with the $10\text{WO}_3\text{-10MoO}_3\text{-80TeO}_2$ glass showing a slightly higher fast neutron removal cross section than the $10\text{WO}_3\text{-20MoO}_3\text{-70TeO}_2$ glass (Ersundu et al., 2018). Specifically, the values reported by the authors ranged from 0.104 to 0.107 cm^{-1} , closely aligning with those obtained in the present study, which focuses on the fabrication of tungsten-free glass systems.

The FNRCs values presented for both glass families, 60TZ and 65TZ, were consistent and mainly depended on the type of added modifier. The values for the prepared samples were quite similar, with the boundaries defined by the TZNa and TZTi samples, which exhibited the lowest and highest values, respectively. Specifically, Na_2O has a specific FNRCs of 0.081 cm^{-1} , while for TiO_2 , the value is 0.139 cm^{-1} (El-Khayatt, 2010). This direct contribution of the individual FNRCs of the oxide in question leads to a higher overall neutron attenuation in the samples containing Ti. Similar behavior accounts for the superior FNRCs observed in the 60/65TZMo sample compared to the 60/65ZBa sample.

5 CONCLUSION

This study concludes that tellurite glasses are highly promising materials for applications in ionizing radiation shielding. The main findings are summarized below, organized logically to integrate the discussed topics:

- **Structural Characterization:** XRD, SEM, and EDS analyses confirmed the development of homogeneous amorphous structures in all samples. XRD revealed broad bands characteristic of amorphous materials, with no evidence of crystallization. SEM images showed smooth and homogeneous surfaces, while EDS indicated a uniform distribution of elements (Te, O, Zn, Mo), consistent with the theoretical compositions.
- **Physical Properties:** Variations in density and oxygen packing density (OPD) were observed among the samples modified with different oxides. BaO-modified glasses exhibited the highest density because of the higher molar mass of barium and its ability to densify the glass network. Conversely, Na₂O-containing glasses showed lower density and higher molar volume, indicative of a more open and less compact structure, consistent with the larger ionic radius and higher mobility of sodium ions.
- **Structural Properties:** Raman spectroscopy identified structural changes associated with the addition of modifying oxides. TiO₂ improved network connectivity through Te–O–Ti bonds, increasing rigidity and thermal stability. MoO₃ introduced MoO₄ and MoO₆ units, increasing the number of non-bridging oxygens (NBO) and structural disorder, while improving radiation absorption. BaO strengthened Te–O–Te bonds, promoting a compact network, while Na₂O increased NBOs, reducing structural cohesion and mechanical stability.
- **Thermal Properties (DSC):** DSC analysis demonstrated that TiO₂ and BaO improved thermal stability, with higher T_g and T_x values, reflecting increased structural densification and crystallization resistance. MoO₃ provided intermediate thermal performance, while Na₂O reduced stability, with lower crystallization onset temperatures.
- **Optical Properties (UV-Vis):** UV-Vis spectroscopy showed that Li₂O and Na₂O improved optical transparency and widened the energy gap (E_g), stabilizing the glass network. MoO₃ reduced E_g by introducing additional electronic states, while TiO₂ demonstrated complex optical behavior due to the coexistence of Ti³⁺ and Ti⁴⁺ states, suggesting potential for selective optical applications.

- **Mechanical Properties:** Vickers hardness tests confirmed that TiO_2 -modified glasses exhibited superior mechanical strength, while Na_2O -modified glasses showed lower hardness, consistent with their more disordered structure. Optical microscopy supported these findings, revealing smooth and defect-free surfaces, indicative of high structural quality.
- **Radiation Shielding Properties:** BaO and MoO_3 significantly enhanced the radiation attenuation properties of tellurite glasses. BaO increased density and cross-linking, improving gamma radiation absorption at low energies. MoO_3 was effective in medium-to-high-energy attenuation due to the introduction of additional electronic states and enhanced Compton scattering. These glasses outperformed conventional materials such as barite concrete and lead glass, highlighting their potential for radiation shielding in high-demand environments.

This study demonstrates the profound influence of intermediate oxides and modifying agents on the structural, physical, thermal, optical, mechanical, and radiation shielding properties of tellurite glasses. The combined use of analytical techniques verified the homogeneous and amorphous nature of the glasses, while the observed property variations suggest that tailored modifications can optimize performance for specific applications.

The glasses modified with TiO_2 , BaO and MoO_3 stood out for their superior thermal stability, mechanical strength, and radiation attenuation capabilities, making them suitable for advanced optical devices and innovative radiation shielding solutions. These findings provide a solid foundation for the development of new tellurite glass compositions designed to meet the demands of modern technological and industrial applications, where performance and reliability are paramount.

6 FUTURE PERSPECTIVES

The findings of this thesis underscore the potential of tellurite glasses as promising materials for applications in ionizing radiation shielding, advanced optical devices, and other high-performance technological applications. To expand the understanding and optimize the properties of these materials, several research directions are proposed:

- **Exploration of New Modifiers and Intermediates:** Investigate the incorporation of alternative metallic oxides or dopants, such as rare-earth oxides (e.g., La_2O_3 , CeO_2) and transition metal oxides (e.g., Ta_2O_5 , Nb_2O_5). These components could further enhance the optical, thermal, mechanical, and radiation-shielding properties of tellurite glasses. Studies focusing on specific combinations of modifiers could enable the tailoring of properties for targeted industrial applications.
- **Performance Evaluation in Real Conditions:** Conduct field tests and performance evaluations under real-world conditions, particularly in high-radiation environments, to validate the effectiveness of tellurite glasses as shielding materials. Comparative analyses with conventional materials, such as lead glass and barite concrete, could quantify efficiency improvements and assess potential cost advantages.
- **Development of New Geometries and Shapes:** Investigate the production of tellurite glasses in various forms, such as thin films, plates, fibers, and composites, to broaden their applicability in optical devices, electronics, sensors, and protective coatings. Research into innovative fabrication techniques, including 3D printing and advanced molding, could optimize the functionality of these glasses in diverse configurations.
- **Computational Simulation and Molecular Modeling:** Apply computational simulations and molecular modeling to predict the behavior of tellurite glasses under various conditions. These approaches could streamline the optimization of compositions and structures at the atomic level, reducing the reliance on extensive empirical experiments and expediting the identification of promising formulations for practical use.
- **Integration with Other Protection Technologies:** Explore the combination of tellurite glasses with complementary materials, such as polymers or composites, to develop hybrid solutions that take advantage of the advantages of each material. These innovations could unlock new possibilities in industries such as aerospace, automotive, medical, and energy.
- **Sustainability and Environmental Impact Studies:** Investigate the environmental implications of tellurite glasses, from production to end-of-life disposal. Future studies

could focus on sustainable manufacturing practices, recycling methods, and strategies to minimize resource use and reduce the carbon footprint associated with production processes.

- **Calculation of Oxide Ion Polarizability:** Detailed analyses of oxide-ion polarizability as a function of the band gap index. This investigation could elucidate the relationship between electronic structure and optical properties, providing insights to optimize glass compositions for maximum transparency and reduced energy losses in optical applications.

These research directions highlight the immense potential of tellurite glasses and provide a roadmap for future exploration aimed at advancing their application in cutting-edge technologies and sustainable solutions.

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APPENDIX A – DEFINITION GLASS

GLASSES

Definition of the Term Glass

Scientifically, classifying a material as glass requires an understanding of its solid-state properties, composition, structure, and the methods used to form it. The first significant study on glass was conducted by Michael Faraday in 1830, who described glass as "a material that resembles a solution of various substances rather than a compound itself" (Alves et al., 2001).

Over time, as our understanding of glass formation and structure has advanced, various definitions have been proposed. This diversity stems from the multiple techniques used to produce glass, beyond the traditional melt-quenching method. A pivotal hypothesis relates to the lack of symmetry in the three-dimensional network of glass. In 1932, Zachariassen published his landmark paper, *The Atomic Arrangement in Glass*, noting the limited understanding of oxide glass structures at the time (Zachariassen, 1932). He proposed that "the atomic arrangement in glasses is characterized by an extended three-dimensional network, which lacks symmetry and periodicity," distinguishing glasses from crystals due to their absence of periodicity and long-range order (Zachariassen, 1932).

As analytical techniques improved, it became clear that the absence of long-range order is a defining property of glass, influencing its structural, physical, thermal, electrical, and optical properties (Manning et al., 2012; Zaki et al., 2018; Al-Ani et al., 2006; Al-Buriahi et al., 2020b). The evolving technological landscape has required a more precise definition of glass. Today, a widely accepted definition is that "glass is an amorphous solid with a complete absence of long-range order and periodicity, exhibiting a glass transition region. Any material, whether inorganic, organic, or metallic, that undergoes a glass transition is considered glass" (Gupta, 1996). Although many researchers have contributed to the definition of glass, these definitions converge on similar fundamental characteristics.

Recent studies suggest that glasses behave as solids for long periods, exhibit mechanical rigidity and elasticity like solids, and fracturing similarly (Al-Buriahi et al., 2020b; Meyers; Chawla, 2008; Cohen-Tannoudji et al., 1973; Torres et al., 2001). However, glasses also flow under gravity at any temperature, transitioning into a supercooled liquid state. Prolonged thermal treatment can induce crystallization in glass. To encompass these nuances, Zanotto and Mauro proposed an updated definition of glass (Zanotto; Mauro, 2017):

Glass is a non-crystalline, thermodynamically non-equilibrium condensed state of matter that exhibits a glass transition. The structures of glasses are similar to those of their supercooled liquids (SCL) and spontaneously relax towards the SCL state. Their ultimate fate, over infinitely long times, is to crystallize.

This definition emphasizes that glasses are amorphous solids lacking symmetry and long-range periodicity, with structures resembling their supercooled liquid counterparts. Despite extensive research, a comprehensive model that describes the interactions within a glassy system remains elusive. However, all definitions consistently highlight the significance of the "glass transition region," which is central to the formation and behavior of glass.

GLASS FORMATION

Early studies on glasses suggested that any combination of components could form glasses, as rapid cooling was believed to prevent crystallization universally. However, as advanced methods emerged and a wider variety of components were tested, it became evident that glass formation was more limited than initially assumed. Glasses, or vitreous systems, are typically formed by cooling molten materials, but can also be produced through alternative techniques, such as vapor phase deposition, sol-gel processing, and irradiation of crystalline materials (Zarzycki, 1991; Shelby, 2020; Wong; Angell, 1976). The melt-quenching process remains the most common method, involving the melting of mixed components at high temperatures near their melting points, followed by rapid cooling. This rapid cooling results in varying the structural arrangements of the molten mixture, depending on the composition and properties of the material (Zarzycki, 1991; Sidek et al., 2009; Gunha et al., 2019).

The first widely studied glass-forming system was the silicate system. Initial research focused on silicate-based glasses before expanding to other types of glass systems. This shift led to the question of why some materials are more easily formed into glass than others, driving the development of various theories of glass formation (Shelby, 2020; Alves et al., 2001; Wong; Angell, 1976).

To understand glass formation, researchers developed structural and kinetic theories. Structural theories focus on the chemical and physical characteristics of glass-forming structures, which explain their ability to form an amorphous state (Boudart; Mariadassou, 1982; Shelby, 2020; Langer, 2014; Scholze, 2012). Kinetic theories emphasize thermal behavior, considering the conditions required to avoid crystallization and enable glass formation (Capanema Junior, 2007; Shelby, 2020; Boudart; Mariadassou, 1982). Historically, structural theories preceded kinetic theories, fostering discussions on the "criteria for vitrification," a concept that will be further explored in Section A.

Structural Theories

Many materials are capable of forming glass today, but identifying universal formation criteria remains a challenge. The oldest theory on glass formation is attributed to Goldschmidt (Zarzycki, 1991), who introduced a stoichiometric approach based on the ratio of cation and oxygen ions, as outlined below:

- ✓ **Goldschmidt Criterion (1926)** (Boudart; Mariadassou, 1982): This criterion attempts to explain vitrification by considering the stoichiometric formula R_nO_m , which relates the ratio of the ionic radius of the cation (R) to that of the oxygen ion. According to this theory, the ratio should lie between 0.2 and 0.4. The coordination number of cations R must align with the criteria for a tetrahedral coordination configuration.

However, a universal application of the Goldschmidt criterion is problematic. For example, while beryllium oxide satisfies the criterion, it does not vitrify (Zarzycki, 1991), demonstrating the limitations of this theory.

Building upon these early ideas, Zachariasen (Zachariasen, 1932) proposed a fundamental distinction between glass-forming and non-glass-forming materials. By reevaluating Goldschmidt work and refining some concepts, Zachariasen formulated a set of rules that significantly advanced glass research. These rules provided a framework for explaining why SiO_2 forms glass while Na_2O does not, and why certain combinations of components can lead to glass formation. From this analysis, Zachariasen established the following principles:

- ✓ The interatomic bond strength and mechanical properties are comparable in glasses and crystals.
- ✓ Crystals form a three-dimensional network, but in glasses, the diffusion of the X-ray spectrum reveals a network without symmetry.

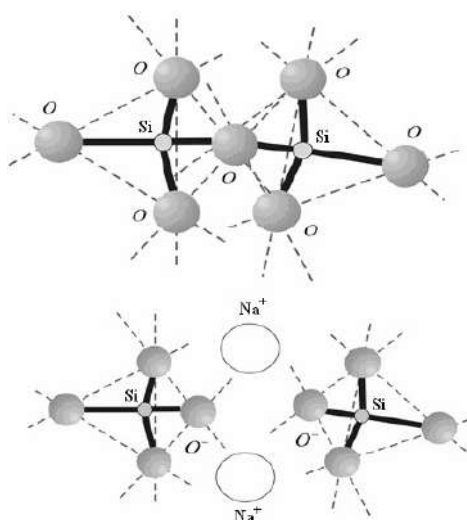
Recognizing that glass formation relies on specific coordination mechanisms, Zachariasen proposed a set of specifications to characterize glass-forming materials. These include:

- Oxygen atoms cannot be bonded to more than two cations.
- The coordination number of oxygen atoms around the cations must be small.
- Oxygen polyhedra should share vertices but not edges.
- Each polyhedron must share at least three vertices with adjacent polyhedra.

- The material should consist of a high percentage of cations surrounded by oxygen in tetrahedral or triangular coordination.
- Tetrahedra or triangles within the network share only one vertex with each other.
- Oxygen atoms precisely link two cations within the network, forming no additional bonds with other cations.

Given these criteria for glass formation, materials are categorized on the basis of their roles within the network: network formers, modifiers, and intermediates. Figure 38 illustrates the effect of a network modifier, Na_2O , on SiO_2 during the glass formation process. The addition of the network modifier disrupts the oxygen bonds between tetrahedra in the Si-O-Si linkages, resulting in the formation of two Si-O^- bonds. For each Na_2O molecule introduced into the network, a Si-O-Si bond is broken. These negatively charged O^- bonds are balanced by Na^+ cations, which facilitates structural reorganization of the vitreous network.

Figure 38 – Si-O-Si bond structure without modification and structure with the formation of a pair of non-bridging oxygens Si-O^- .



Source: Adapted (Zachariasen, 1932).

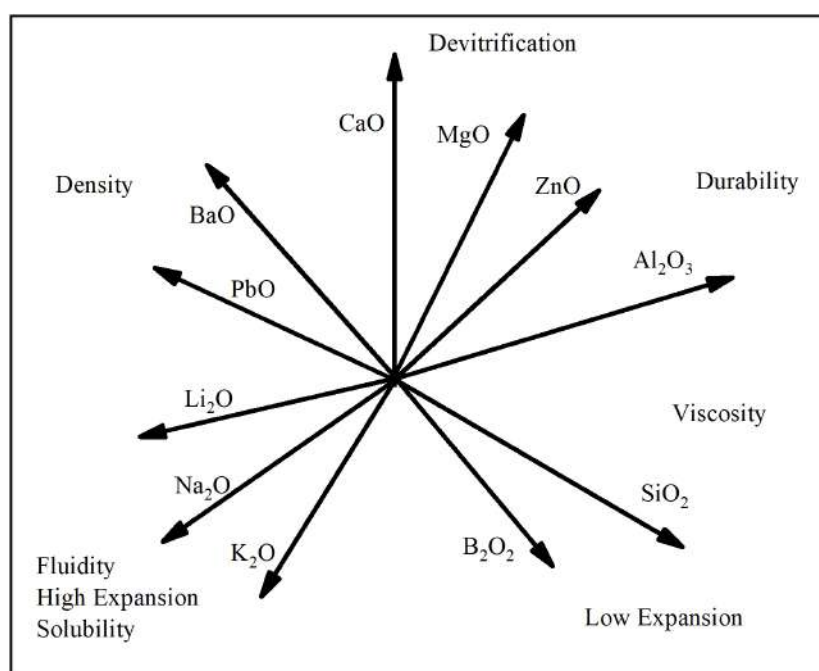
In 1952, Stanworth proposed a new criterion (Stanworth, 1952) suggesting that the bonding strength within a vitreous network is significantly influenced by the covalent nature and orientation of the oxides. This theory emphasizes that the degree of bond ionicity is determined by the difference in electronegativity between the bonding elements: The smaller the difference, the stronger the bond. Given that oxygen has an electronegativity of 3.5, cations can be classified into the following categories:

- * Electronegativity between 1.8 and 2.1 is the former of the network (e.g. $\text{Si} = 1.8$).
- * Electronegativity between 1.5 and 1.8 is intermediate (e.g., $\text{Al} = 1.5$).

* Electronegativity less than 1.5 is a network modifier (e.g., Mg = 1.2 and Ca = 1.0).

A review of the literature highlights the significant variations in properties exhibited by oxides as a result of their diverse chemical compositions. For example, as illustrated in Figure 39, the incorporation of certain oxides, such as BaO and PbO, improves the density of the glass while simultaneously reducing its viscosity (Zachariasen, 1932; Giehl, 2011; Stambouli et al., 2012; Ghribi et al., 2015).

Figure 39 – Diagram showing the influence of adding specific oxides on the properties of the glass.



Source: The author.

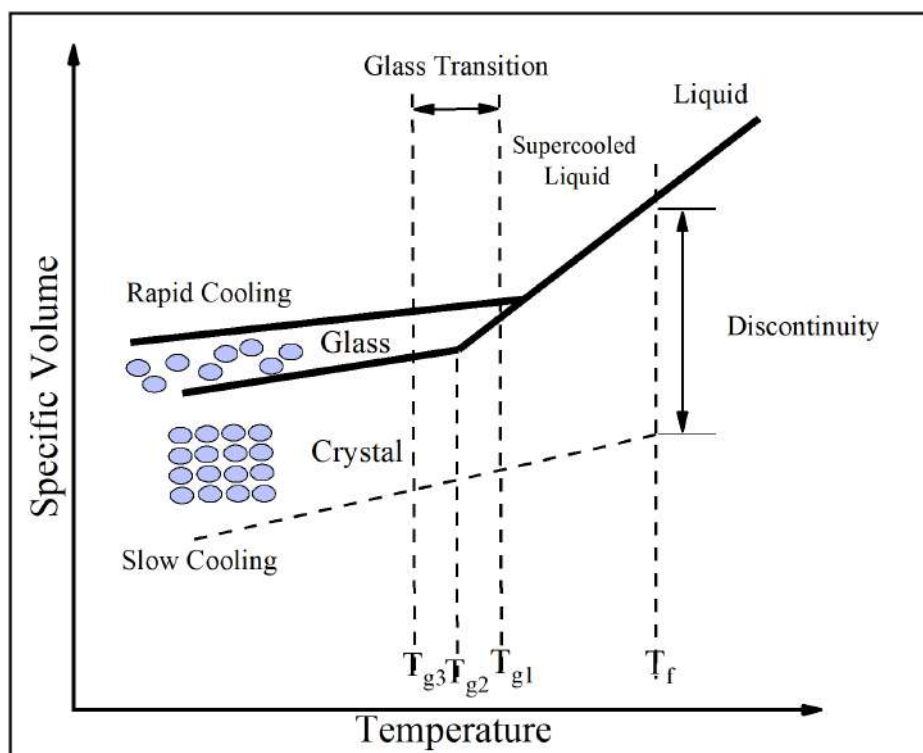
However, the criteria and rules discussed so far are insufficient to fully explain the complexities of glass formation. A crucial additional factor to consider is the dynamics of vitreous network formation, which will be introduced in the next section of the kinetic theories. Only through the integration of both structural and kinetic perspectives can a comprehensive understanding of the processes involved in the formation of a vitreous network be obtained.

Kinetic Theory

Kinetic theory explains glass formation as a result of the resistance of the materials to crystallization during cooling. In this framework, glass formation is conceptualized as a competition between the cooling and crystallization rates (Köster; Herold, 2005; Shelby, 2020).

Conventional glasses are typically produced using the melt-quenching method. During cooling, the material can undergo a glass transition or crystallize, depending on the cooling rate and other factors (Giehl, 2011). The relationship between the liquid and the resulting glass can be illustrated using the volume-temperature diagram shown in Figure 40.

Figure 40 – Change in volume during cooling and its influence on the glass transition temperature.



Source: The author.

For a vitreous system to form, the cooling rate must be rapid. If the cooling process is slow, the material has enough time to reorganize into a periodic structure, resulting in crystallization rather than glass formation. As mentioned above, glass is defined as a material lacking periodicity and symmetry (Zarzycki, 1991; Shelby, 2020).

The volume-temperature diagram (Figure 40) illustrates this process, starting from the liquid equilibrium state as the temperature decreases to the melting temperature (T_f). At T_f , two outcomes are possible: the material may crystallize, typically accompanied by a discontinuous volume contraction, or it may transition to a supercooled state. If no significant volume change occurs at T_f and the cooling rate remains consistent, the liquid enters a metastable supercooled region, where minor perturbations can still induce crystallization (Idalgo Júnior, 2005).

For crystallization to occur, the molecules need time to orient and relax into a periodic arrangement. However, with rapid cooling, the molecular mobility is reduced, trapping the liquid in a metastable state. As the temperature decreases further, molecular movements become increasingly restricted, leading to the formation of a disordered

network near the glass transition temperature (T_g) (Ghribi et al., 2015).

The glass transition region marks the onset of structural relaxation, where molecular mobility becomes immobilized. The glass transition temperature (T_g) depends on the cooling rate— T_{g1} represents higher cooling rates, while T_{g3} corresponds to slower rates. When the cooling rate is sufficiently rapid, the material follows the vitrification path instead of the crystallization path, and it can only be classified as glass below T_g (El-Mallawany, 2016).

Thus, rapid cooling is a fundamental requirement for glass formation, preventing the reorganization needed for crystallization. This emphasizes the importance of determining the optimal cooling rate for effective glass formation and controlling crystallization, which occurs through two primary mechanisms: crystal growth and nucleation.

Crystallization

Crystallization occurs during slow cooling, producing a network with symmetry and order from the molten material. To understand this process, it is essential to examine the mechanisms of nucleation and crystal growth (Patra; Annapurna, 2022).

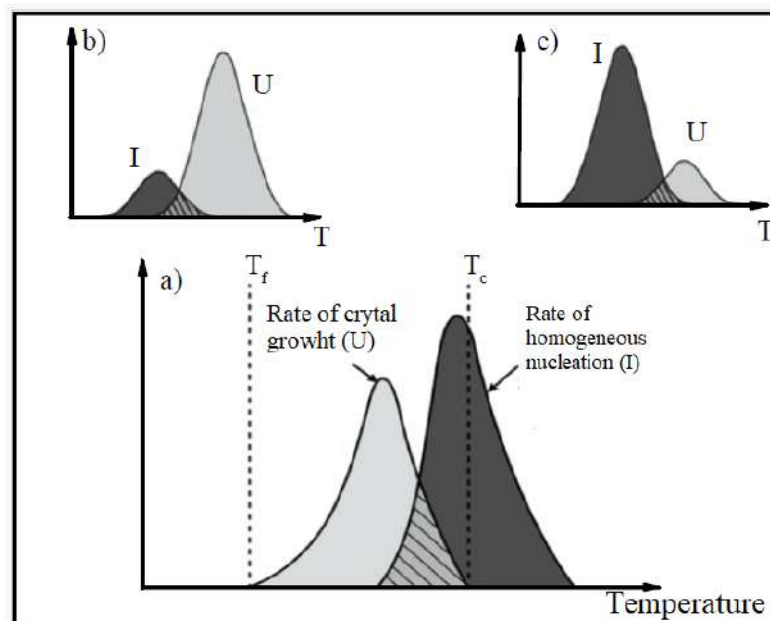
Nucleation is the phase where the system begins to organize itself at specific points, forming what are known as nuclei. Crystal growth follows, during which these nuclei expand. Although both stages may occur simultaneously, they are governed by distinct rate laws. Nucleation is particularly critical because, in its absence, crystallization cannot take place. In contrast, if the nuclei do not grow, they remain of imperceptibly small size (Idalgo Júnior, 2005; Ghribi et al., 2015).

The interplay between nucleation and growth rates, combined with the cooling rate, ultimately determines whether glass formation is possible. The resistance of a glass to crystallization upon reheating is referred to as its glass stability. Both the number of nuclei produced per unit volume over time and the growth rate of these nuclei are temperature dependent, as illustrated in Figure 41.

Some insights into the dependence of the nucleation (**I**) and growth (**U**) rate curves, as proposed by Zanotto (Zanotto; Materials, 1990), are as follows:

- ✓ Small hatched region: When the overlap between the curves is minimal, crystallization is unlikely to occur.
- ✓ Significant overlap with high rates: If the hatched region is extensive and both the nucleation (**I**) and growth (**U**) rates are high, complete crystallization of the material is possible.
- ✓ High nucleation, low growth: When the nucleation rate is high but the growth rate is low within the hatched region, a partially crystalline material with small, dispersed crystals is formed.

Figure 41 – Schematic diagram illustrating the possible mechanism of glass crystallization.



Source: Source: Adapted (Patra; Annapurna, 2022).

- ✓ Low nucleation, high growth: If the nucleation rate is low and the growth rate is high, the material will exhibit a small number of large crystals within an amorphous matrix.

APPENDIX B – BRIEF HISTORY RADIATION

RADIATION

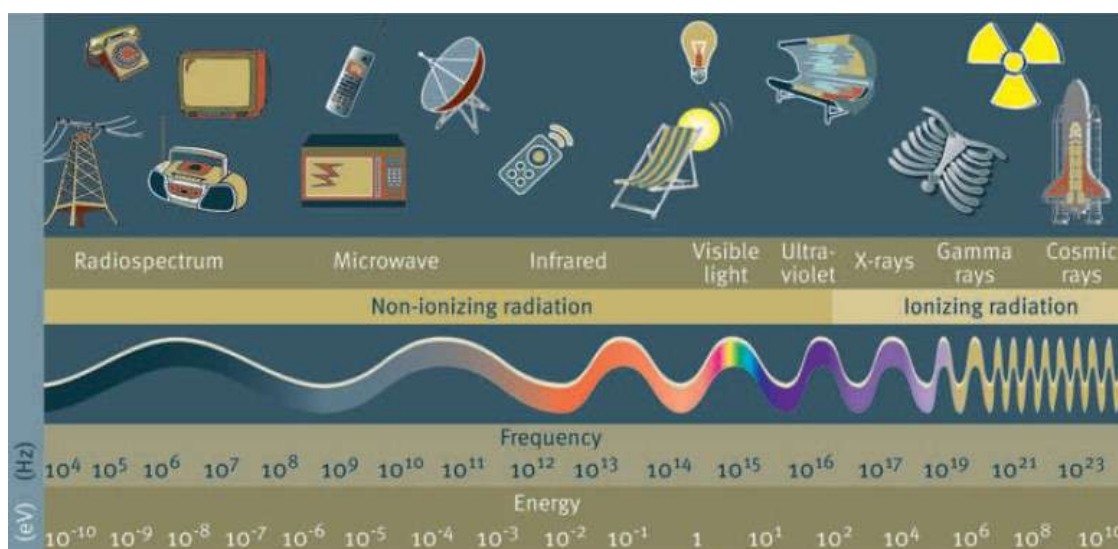
Radiation is an integral part of our daily lives, from natural background radiation in our environment to cutting-edge technologies that rely on it in fields like medicine and engineering. A comprehensive understanding of radiation is crucial for professionals in nuclear sciences and related fields, as well as for the general public, to make informed decisions about safety and exposure.

Radiation exists in various forms and is everpresent. Although the terms radioactivity, nuclear energy, and atomic energy are commonly associated with radiation, they also encompass a broader spectrum, including radio and television signals, ultraviolet radiation, infrared radiation, and even sound and visible light.

A deeper understanding of these different types of radiation and their applications enables us to exploit their beneficial properties while mitigating associated risks. For example, ultraviolet (UV) radiation is vital for the synthesizing of vitamin D in the skin but can also damage cellular DNA, potentially causing skin cancer. Infrared (IR) radiation, in contrast, has widespread applications in thermal imaging and heating technologies.

Figure 42 illustrates the diverse applications of radiation in various domains.

Figure 42 – Examples of different types of applications utilizing radiation.



Source: Adapted (UNEP, 2016).

A BRIEF HISTORY OF RADIATION

The discovery and study of radiation represent a pivotal milestone in science that profoundly influences fields such as medicine, physics, chemistry, and engineering. Below is an overview of key milestones in the history of radiation:

- **1895:** Wilhelm Conrad Roentgen discovered X-rays while experimenting with cathode ray tubes. He observed that an unknown type of radiation could penetrate opaque materials and produce images on photographic plates, revolutionizing medicine by allowing visualization of the interior of the human body without invasive procedures (Röntgen, 1896).
- **1896:** Henri Becquerel discovered radioactivity, noting that uranium salts could darken covered photographic plates even without exposure to sunlight. This discovery revealed that certain materials emit radiation spontaneously (Becquerel, 1896).
- **1898:** Marie and Pierre Curie isolated polonium and radium from uranium ore, advancing the understanding of radioactivity. Their groundbreaking work earned them the Nobel Prize in Physics in 1903 and laid the foundation for modern radiological science (Curie; Sklodowska-Curie, 1898).
- **1905:** Albert Einstein theory of special relativity introduced the equation $E = mc^2$, which demonstrates the equivalence of mass and energy. This insight was critical for understanding the energy released in radioactive decay and nuclear reactions.
- **1911:** Ernest Rutherford proposed a new atomic model based on alpha-particle scattering experiments, revealing a dense, positively charged nucleus surrounded by orbiting electrons. This model was instrumental in understanding nuclear processes (Rutherford, 1911).
- **1934:** Irène and Frédéric Joliot-Curie discovered artificial radioactivity, showing that non-radioactive elements could be made radioactive through alpha-particle bombardment. This discovery significantly expanded the applications of radioactivity (Joliot; Curie, 1934).
- **1942:** Enrico Fermi and his team achieved the first controlled nuclear chain reaction at the University of Chicago, marking a milestone in nuclear energy development and leading to the construction of the first nuclear reactors (Sekimoto, 2008; Gu, 2018).
- **1945:** The atomic bombings of Hiroshima and Nagasaki demonstrated the destructive potential of nuclear fission, ending World War II but underscoring the urgent need for regulating nuclear technology.

- **1954:** The world first commercial nuclear power plant was opened in Obninsk, Soviet Union, initiating the large-scale use of nuclear energy for electricity generation.
- **1970s-1980s:** Advances in medical imaging technologies, such as Positron Emission Tomography (PET) and Magnetic Resonance Imaging (MRI), transformed diagnostics and treatment by providing detailed insights into physiological and anatomical processes (Phelps, 2000; Lauterbur, 1973).
- **Present:** Nuclear energy continues to advance with safer and more efficient reactors, while radiation protection and regulation have become critical for ensuring safety in environments that utilize radiation.

The history of radiation is marked by groundbreaking discoveries and transformative technologies that have reshaped science and society. From X-rays and radioactivity to nuclear energy and advanced medical imaging, radiation remains central to scientific progress, medicine, and industry, addressing challenges and opportunities across diverse applications.

ELECTROMAGNETIC RADIATION

Electromagnetic radiation encompasses a wide range of energies, collectively known as the electromagnetic spectrum. This spectrum includes various forms of radiation, such as gamma rays, X-rays, ultraviolet, visible light, infrared, microwaves, and radio waves. Each type of radiation has distinct properties, including wavelength, frequency, and energy. Maxwell's equations govern the relationship between these properties, explaining how electromagnetic radiation propagates as waves, carrying electric and magnetic components generated by moving charged particles, such as electrons.

Electromagnetic radiation is mainly characterized by two parameters: wavelength (λ) and frequency (f). These parameters are inversely proportional: shorter wavelengths correspond to higher frequencies, while longer wavelengths correspond to lower frequencies. Wavelength refers to the distance between two consecutive peaks or troughs of a wave, while frequency, measured in hertz (Hz), indicates the number of wave cycles passing a specific point per second (Fermi, 1950; Tipler; Mosca, 2007).

The electromagnetic spectrum encompasses all forms of electromagnetic radiation, organized by increasing frequency or decreasing wavelength. The primary regions of the spectrum include:

- **Radio Waves:** Possess the longest wavelengths and the lowest frequencies. They are widely used in communications, broadcasting, and radar applications.

- **Microwaves:** Have slightly shorter wavelengths than radio waves and are used in microwave ovens, wireless communication, and satellite transmissions.
- **Infrared Radiation (IR):** Feature shorter wavelengths than microwaves and are used in thermal imaging, remote controls, and certain communication technologies.
- **Visible Light:** The only portion detectable by the human eye, ranging from violet (shortest wavelength, highest frequency) to red (longest wavelength, lowest frequency). It is essential for illumination and human vision.
- **Ultraviolet Radiation (UV):** Exhibits shorter wavelengths than visible light and is used in sterilization, fluorescence applications and tanning, but can also cause sunburn.
- **X-Rays:** Possess higher energy and shorter wavelengths than UV rays. They are used in medical imaging, security screening, and material analysis.
- **Gamma Rays:** Have the highest energy and the shortest wavelengths. They are applied in medical diagnostics, cancer treatment, and scientific research.

Electromagnetic waves can propagate through vacuum and through various media, including air, water, and solids. In a vacuum, all electromagnetic waves travel at the speed of light, denoted by c , which is approximately 299.792 km/s. Electromagnetic radiation exhibits both wave-like and particle-like behaviors: It can interfere with itself, diffuse around obstacles, and exhibit polarization. It is made up of energy packets known as photons. The energy of a photon is directly proportional to its frequency and inversely proportional to its wavelength, as described by the Planck-Einstein relation:

$$E = hf \tag{B.1}$$

where h is the Planck constant, approximately 6.626×10^{-34} J·s (Fermi, 1950; Tipler; Mosca, 2007).

INTERACTIONS OF IONIZING RADIATION WITH MATTER

Ionization, Excitation, Activation, and Bremsstrahlung Radiation

When ionizing radiation interacts with matter, it can trigger various processes such as atomic or molecular excitation, ionization, or nuclear activation. The specific interaction depends on the energy and nature of the radiation.

In **atomic or molecular excitation**, radiation causes electrons to move from their equilibrium orbitals to higher energy states. These excited electrons subsequently

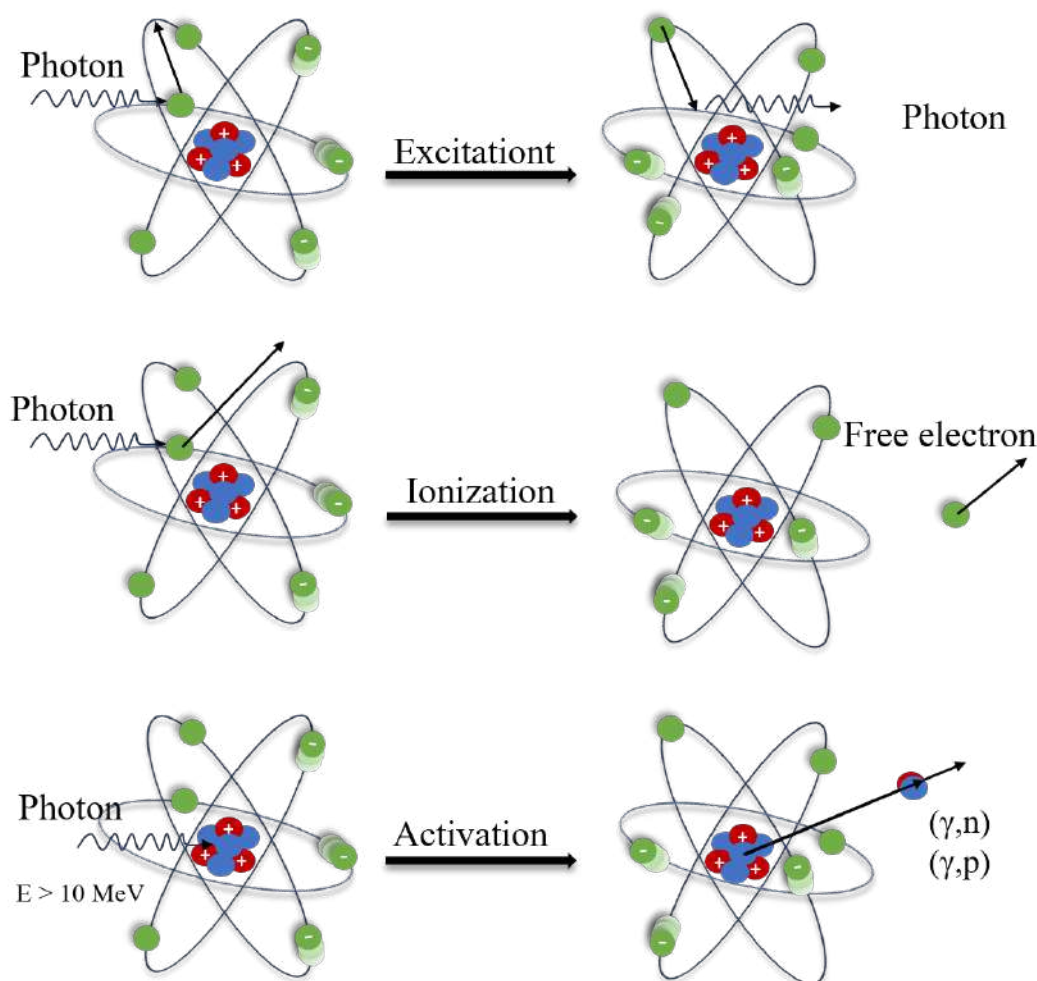
release excess energy in the form of light or X-rays, a phenomenon commonly observed in materials exposed to radiation.

In **ionization**, radiation possesses sufficient energy to remove electrons from atomic orbitals, creating high-energy free electrons, positive ions or free radicals. This process is particularly significant because it can break chemical bonds and alter the physical and chemical properties of the irradiated material (Attix, 2008).

In **nuclear activation**, high-energy radiation interacts with the nucleons (protons and neutrons) of an atom, overcoming the binding energy to induce nuclear reactions. This results in a residual nucleus and radiation emission. A common occurrence is the absorption of low-energy, or thermal, neutrons, which depends on the material's composition and its neutron capture cross-section. When a nucleus captures a neutron, it enters an excited state, emitting characteristic radiation as it de-excites.

Figure 43 provides a detailed diagram that illustrates these interaction processes, highlighting the various pathways through which ionizing radiation interacts with matter.

Figure 43 – Illustrative scheme of the different modes of radiation interaction with matter.



Source: The author.

Lastly, but not least, **bremsstrahlung radiation** occurs when charged particles, such as alpha particles, beta particles, and accelerated electrons, interact with matter and release a portion of their kinetic energy as electromagnetic radiation. Approximately 5% of this energy is converted into bremsstrahlung X-rays, a type of radiation generated by the interaction of the electric fields of the incident particles, nuclei, and atomic electrons. This process is more likely in interactions involving electrons and atoms with high atomic numbers, as the exit angle of the particles is random and the energy converted into X-rays ranges from zero to the maximum value corresponding to the kinetic energy of the incident particle (Tsoulfanidis; Landsberger, 2021).

Directly and Indirectly Ionizing Radiations

Radiation can be classified as **directly** or **indirectly ionizing** based on its interaction with materials during the energy transfer process.

Directly ionizing radiations, such as electrons, alpha particles, and fission fragments, primarily interact through their electric fields, transferring energy to many atoms simultaneously. This type of radiation causes ionization directly as it travels through matter.

Indirectly ionizing radiations, such as neutrons, X-rays, and other forms of electromagnetic radiation, are not charged. These radiations interact indirectly by transferring their energy to electrons, which subsequently cause ionization. Due to this mode of interaction, indirectly ionizing radiation can penetrate deeply and pass through significant thicknesses of the material without substantial interaction (Knoll, 2010).

The term "*interaction*" for indirectly ionizing radiation, such as photons and neutrons, refers to processes that alter the direction or energy of the radiation. These processes occur randomly, meaning their occurrence is not deterministic, but their probability can be calculated. The likelihood of radiation interacting with a specific material is determined by the **cross-section**, which represents the probability of interaction per unit of particle fluence relative to the number of interaction centers (nuclei, electrons, or atoms) in the material.

The term *fluence* describes the number of particles passing through a specific area. The cross-section (σ) represents the apparent area an interaction center presents for incident radiation to interact with it, measured in units of $[L^2]$. In the International System (SI), the standard unit is square meter (m^2). However, due to the scale of nuclear interactions, the unit **barn** (b) is commonly used, where $1 \text{ barn} = 10^{-28} m^2$ (Lamarsh, 2001; Tsoulfanidis; Landsberger, 2021).

INTERACTION OF ELECTROMAGNETIC RADIATION WITH MATTER

X-rays and gamma rays are the most important ionizing electromagnetic radiations. These radiations have a high penetrating power in matter because they are wave-like, have no electric charge, and possess no rest mass. The probability of absorption or scattering events determines the penetration depth of these radiations (Knoll, 2010).

The penetrability of X-rays and gamma rays far exceeds that of charged particles. Furthermore, the energy value of the interaction is directly related to its probability. Photonuclear reactions can occur when the photon energy exceeds the binding energy of nucleons, which is approximately 8.5 MeV. Giant resonance photonuclear reactions are observed when electromagnetic radiation enters the energy range of 10 to 50 MeV, allowing activation of most chemical elements with which it interacts (Attix, 2008).

The primary mechanisms through which electromagnetic radiation interacts with matter, excluding nuclear reactions, include the **photoelectric effect**, **Compton effect**, and the **pair production**. These processes involve the transfer of energy from the photon to the material. Depending on the energy of the photons and the properties of the irradiated material, various forms of absorption and scattering occur, resulting in distinct interaction phenomena (Turner, 2008).

Photoelectric Effect

The complete transfer of energy from an X-ray or gamma photon to a single orbital electron is known as the photoelectric effect, which results in the ejection of this electron from the atom with a precise kinetic energy (E_c). In this process, the photon is completely absorbed and disappears. The kinetic energy of the electron can be expressed as:

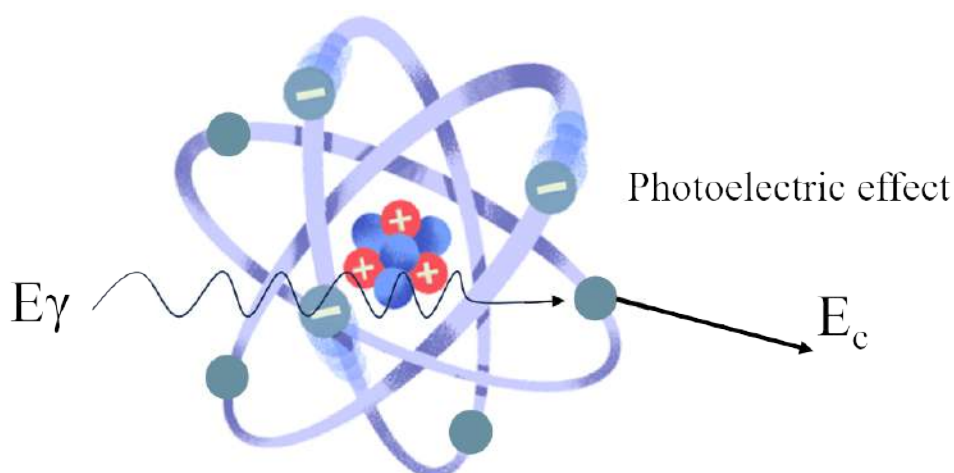
$$E_c = h \cdot \nu - B_e \quad (\text{B.2})$$

where h is Planck constant, ν is the frequency of the radiation, and B_e is the binding energy produced when an electron binds to the orbital (Heisenberg, 1949; Eisberg; Resnick, 1986).

The binding energy (B_e) is a constant value that separates the kinetic energy (E_c) of the ejected electron from the original photon energy. The interaction allows the photoelectric effect, which transfers the electron energy to the material of a detector, to identify and determine the energy of the incident photon. Figure 44 illustrates the photoelectric effect process, showing how radiation interacts with the orbital electron and subsequently emits the electron with a specific kinetic energy.

The energy alters the exit direction of the photoelectron in relation to the incidence of the photon. The probability that an electron exits in the same direction as the photon

Figure 44 – Illustrative Diagram of the Photoelectric Effect



Source: The author.

is higher at high energies (above 3 MeV). However, at low energies (below 20 keV), it is more likely to exit at an angle of approximately 70 degrees ¹.

This occurs because the electric and magnetic fields move perpendicularly to the propagation direction of the photon and exert force on the electron at an angle. As a result, the electron angular momentum is formed by these fields ² (Eisberg; Resnick, 1986; Heisenberg, 1949; Knoll, 2010).

Chemical elements with a high atomic number (Z) and low energies exhibit the photoelectric effect. The probability of occurrence increases with Z^4 and decreases rapidly with increasing energy. The photoelectric effect predominates in lead for energies below 0.6 MeV and in aluminum for energies below 0.06 MeV. It is most likely for electrons in the K, L, and M shells of the same atom (Knoll, 2010).

Compton Effect

The Compton effect describes the interaction between a photon with fixed energy and a loosely bound electron during which the photon transfers a portion of its energy to the electron. This process results in the photon being scattered in a different direction with reduced energy, while the ejected electron gains variable kinetic energy ranging from

¹ The transfer of energy from an ionizing electron to the surrounding material generates secondary ionizations proportional to the transferred energy. Consequently, the amplitude of the voltage pulse or the intensity of the current generated by the collection of electrons and ions at the end of the process directly reflects the energy of the incident radiation. This mechanism is fundamental in the operation of radiation detectors, where the magnitude of the generated electrical signals is used to measure and identify the energy of the radiation that interacted with the detector material.

² The range of a photoelectron with an energy of 1 MeV varies depending on the material in which it propagates. In sodium iodide crystal doped with thallium (NaI(Tl)), a material widely used in the construction of radiation detectors, the range of the photoelectron is approximately 1.8 mm. In contrast, in germanium (Ge), another common material in detectors, the range is reduced to about 0.8 mm. These differences reflect the absorption and interaction properties of each material, which influences the efficiency and accuracy of radiation detectors in various applications

zero to a maximum value. The energy of the scattered photon depends on the scattering angle, θ .

The relationship between the scattered photon energy, E'_γ , the incident photon energy, E_γ , and the scattering angle, θ , is expressed as follows, where $\alpha = \frac{E_\gamma}{m_0 c^2}$ (Compton, 1923; Heisenberg, 1949; Eisberg; Resnick, 1986):

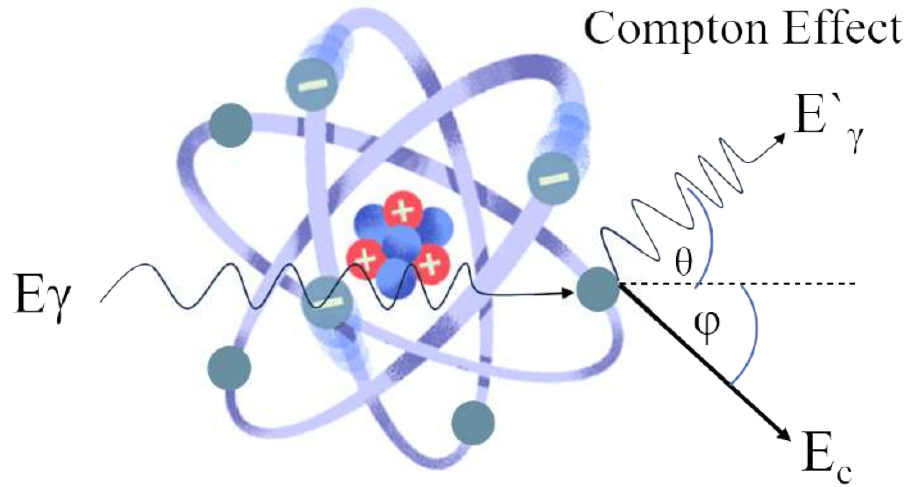
$$E'_\gamma = \frac{E_\gamma}{1 + \alpha(1 - \cos \theta)} \quad (\text{B.3})$$

The energy of the scattered photon is maximized at $\theta = 0^\circ$ and minimized at $\theta = 180^\circ$. At $\theta = 180^\circ$, the ejected electron achieves its maximum kinetic energy, calculated as:

$$T_{\max} = E_\gamma \frac{2\alpha}{1 + 2\alpha} \quad (\text{B.4})$$

Figure 45 illustrates the Compton effect. When the binding energy of the orbital electron is significantly lower than the incident photon's energy, the probability of Compton scattering increases. This effect becomes dominant at higher gamma-ray energies or when the electron binding energy is negligible compared to the photon energy.

Figure 45 – Schematic representation of the Compton effect.



Source: The author.

The Compton effect can be described using an analogy to a mechanical collision, enabling the derivation of expressions for the energy of the scattered photon and the kinetic energy of the ejected electron as functions of the scattering angle and emission angle, respectively. In this formalism, the photon exhibits particle-like behavior, while the electron is treated as a free particle. These simplifications provide practical approximations but lack the full quantum mechanical rigor required for a complete description (Compton, 1923; Heisenberg, 1949; Eisberg; Resnick, 1986).

The Compton scattering cross-section, describing the probability of such events, involves two intermediate processes (Cohen-Tannoudji et al., 1973):

- The photon with energy $E_\gamma = h\nu_0$ is absorbed by the electron, which transitions to an intermediate state with momentum $h\nu_0/c$. The electron emits a photon with energy $E'_\gamma = h\nu'$ during its transition to the final state.
- The electron in the intermediate state, with momentum $-h\nu'/c$, absorbs the photon $h\nu_0$ and transitions to its final state.

For low-energy photons interacting with tightly bound electrons, coherent scattering, or the Rayleigh effect, may occur. In this case, the atom absorbs the recoil, resulting in a directional change of the photon without significant energy loss. The Rayleigh effect is more likely for low-energy photons and elements with high atomic numbers. For example, in carbon, the Rayleigh effect contributes up to 15% of the total radiation attenuation for photons in the 20 keV energy range. Although the Rayleigh effect is distinct in its mechanism, it can be considered a specific case of Compton scattering, characterized by coherent interaction and minimal energy loss (Knoll, 2010).

Pair Production

Pair production is a predominant interaction mechanism for high-energy electromagnetic radiation, which occurs when photons with energy greater than 1.022 MeV interact near nuclei with a high atomic number. The strong electric field of the nucleus facilitates this interaction, during which the photon disappears, and an electron-positron pair is created. This process requires a minimum energy of $2mc^2 = 1.022$ MeV, corresponding to the combined rest mass of the electron and positron (Evans; Evans, 1955; Knoll, 2010). The reaction can be represented as:

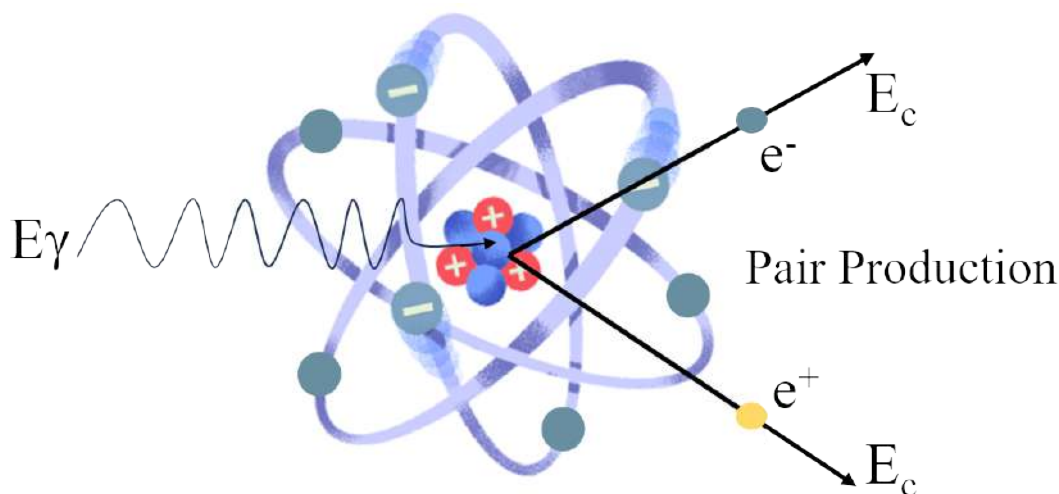
$$\gamma \rightarrow e^- + e^+ + \text{Kinetic Energy} \quad (\text{B.5})$$

The produced electrons and positrons transfer their kinetic energy to the surrounding material through interactions. Eventually, the positron loses its energy and undergoes annihilation by combining with an electron from the medium. This annihilation results in the production of two gamma photons, each with an energy of 511 keV. These annihilation photons contribute to the detection signal in radiation detection systems, as illustrated in Figure 46.

When pair production occurs in a radiation detector, the escape of one or both annihilation photons can significantly impact the detected energy spectrum. Depending on the detector dimensions, the following spectral features may be observed:

- **Total Peak:** corresponding to the complete detection of the incident photon's energy, with no annihilation photon escape.
- **Single Escape Peak:** Occurs when one annihilation photon (511 keV) escapes the detector, resulting in a peak with energy reduced by 511 keV.

Figure 46 – Illustrative diagram of the pair production process.



Source: The author.

- **Double Escape Peak:** Occurs when both annihilation photons escape, leading to a peak reduced by 1.022 MeV (Khan; Gibbons, 2014; Tsoulfanidis; Landsberger, 2021).

At low photon energies, the photoelectric effect dominates as the primary interaction mechanism. However, as the photon energy increases, the probability of the photoelectric effect decreases rapidly, and the Compton effect becomes the dominant process. At even higher photon energies, pair production supersedes the Compton effect as the predominant interaction. Figure 47 illustrates how the relative importance of these processes varies with the photon energy and the atomic number (Z) of the material.

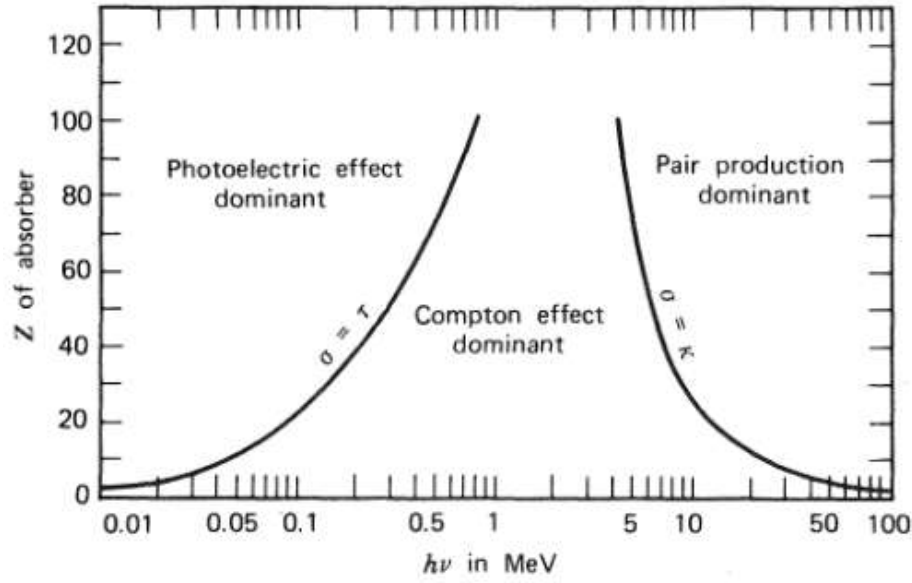
Neutron Interaction with Matter

The interaction of neutrons with matter is a fundamental phenomenon in nuclear physics, with applications in nuclear reactors, medicine, and material analysis. Unlike charged particles, neutrons primarily interact through nuclear forces, allowing them to engage directly with atomic nuclei in complex ways. These interactions depend on the neutron energy, the nature of the target material, and the specific characteristics of the interaction, enabling neutrons to penetrate deep into matter. The two primary types of neutron interaction with matter are scattering and absorption.

Scattering: In the scattering process, a neutron collides with a nucleus, exchanging energy while remaining free after the interaction. Scattering can occur elastically or inelastically:

- **Elastic Scattering:** The neutron transfers part of its kinetic energy to the nucleus, but the total kinetic energy of the system is conserved. Elastic scattering is particu-

Figure 47 – Relative importance of photon interaction processes with matter as a function of photon energy and the material atomic number (Z).



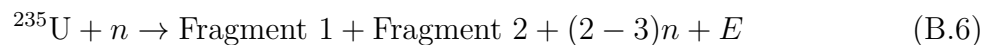
Source: (Winch et al., 2017).

larly prevalent in light nuclei, such as hydrogen, and is fundamental for moderating neutrons in nuclear reactors.

- **Inelastic Scattering:** The neutron is temporarily captured by the nucleus, forming a compound nucleus in an excited state. The nucleus then emits low-energy neutron and gamma radiation. In this process, a portion of the neutron's kinetic energy is converted into the nucleus's excitation energy (Shultis et al., 2016).

Absorption: In absorption, the neutron is captured by the nucleus, leading to the formation of new nuclei or the emission of other particles. Common absorption processes include:

- **Radiative Capture (n, γ):** The neutron is absorbed and the nucleus emits a gamma photon, forming a new isotope, often radioactive. The cross-section, which measures the effective area of the nucleus for neutron capture, represents the probability of this process (Fermi, 1950; Stacey, 2007).
- **Nuclear Fission (n, f):** Fission occurs in fissile nuclei, such as ^{235}U , ^{233}U , and ^{239}Pu . A neutron is captured, causing the nucleus to become unstable and split into two fragments, releasing energy and additional neutrons. The reaction is represented as:



Here, E is the energy released during fission, typically around 200 MeV. This energy is distributed among the kinetic energy of the fragments, the gamma radiation, the neutron energy, and the energy of the decay product (Krane, 1991).

Neutron Energy Dependence: Neutron interactions vary significantly with neutron energy:

- **Thermal Neutrons (Energy ~ 0.025 eV):** These have a high probability of being captured by nuclei due to resonance cross-sections at low energies.
- **Fast Neutrons (Energy > 1 MeV):** These are more likely to undergo scattering interactions, with a lower probability of capture.
- **Intermediate Energies:** At these energies, specific nuclear resonances occur, causing a dramatic increase in the capture cross-section, which significantly influences the rate of nuclear reactions (Knoll, 2010).

Applications: The unique properties of neutron interactions have diverse applications:

- **Nuclear Reactors:** Thermal neutrons sustain the fission reaction, whereas moderators like water and graphite reduce the neutron energy to the optimal range.
- **Material Analysis:** Neutron activation analysis identifies elements through neutron capture and the emission of characteristic radiation.
- **Radiation Shielding:** Materials such as water, concrete, and hydrogen-rich polymers are used to slow and absorb neutrons, providing effective shielding (Lamarsh, 2001).

In summary, neutron interactions with matter are complex and depend on the neutron energy and material composition. These interactions underpin critical technologies in energy, science, and medicine, highlighting the importance of understanding their fundamental principles.

DANGERS OF IONIZING RADIATION AND PROTECTION PRINCIPLES

Ionizing radiation, because of its ability to ionize atoms and molecules, can cause significant cellular damage, primarily to DNA. These lesions can cause genetic mutations, cell death, and serious health issues such as cancer. Acute exposure to high radiation doses can result in immediate effects, including burns and acute radiation syndrome, while prolonged exposure increases the risk of long-term effects, such as cancer development.

Radiological protection is based on three essential principles: time, distance, and shielding. Since the radiation dose received is directly proportional to the exposure time to a radiation source, minimizing exposure time is crucial. The inverse square law demonstrates that the intensity of the radiation decreases significantly with increasing distance from the source (Lamarsh, 2001; Knoll, 2010):

$$D_1 r_1^2 = D_2 r_2^2 \quad (\text{B.7})$$

where D_1 and D_2 represent radiation doses at distances r_1 and r_2 from the source, respectively. This principle ensures that personnel and equipment remain at safe distances from radiation (Protection, 2007; Cousins et al., 2011; Shultis et al., 2016).

To reduce the radiation dose received, appropriate shielding materials such as lead, concrete, or polyethylene are essential. Dense materials such as lead are particularly effective against gamma rays, while hydrogen-rich materials like concrete and polyethylene provide excellent protection against neutrons.

When selecting shielding materials, it is important to consider the type and energy of the radiation as well as the desired level of protection. Although materials like concrete and water are effective and economical, high-density polyethylene may be preferred in applications where space is limited.

Figure 48 illustrates the penetration power of various types of radiation, using Cobalt-60 as an example. Cobalt-60, which decays to nickel-60, emits gamma photons and requires appropriate shielding to effectively minimize radiation exposure. The figure highlights the main forms of interaction, including ionization, scattering, and absorption, and the corresponding ideal shielding materials for each type of radiation.

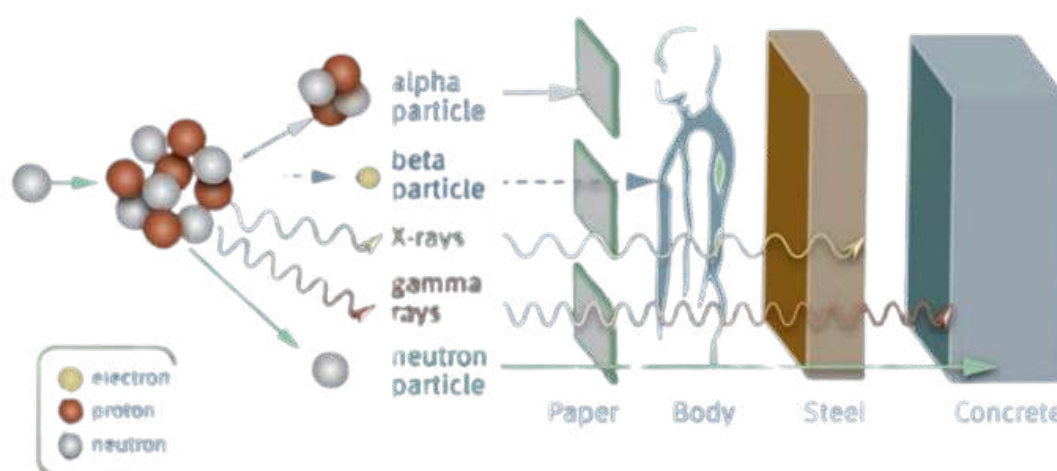


Figure 48 – Illustration of the penetrating power of different types of radiation and the ideal shielding materials for Cobalt-60, which decays to nickel-60, emitting gamma photons.

Source: Adapted from (UNEP, 2016).

APPENDIX C – THE IMPACT OF GLASS COMPOSITION ON RADIATION SHIELDING EFFECTIVENESS

INTRODUCTION

In this chapter, we explore radiation shielding simulations using matrices previously investigated by the Grupo de Propriedades Eletrônicas e Vibracionais em Materiais (GPEVIM). These matrices were selected based on comprehensive analyses of their structural, thermal, and optical properties, as detailed in dissertations, theses, and publications from the group (Piazzetta, 2015; Gomes Junior, 2015; Gonçalves et al., 2016; Gonçalves, 2016; Gomes et al., 2018; Gunha et al., 2019; Gunha et al., 2019; Novatski et al., 2019; Gomes Junior, 2019; Gunha, 2020; Gonçalves, 2021).

Recent studies have provided further information about these materials, focusing on their potential for radiological protection. Modifications involving oxides and fluorides, such as LiF and ZnF_2 , have been investigated to improve chemical stability and reduce moisture absorption, a recurring limitation in conventional glasses. These efforts highlight the importance of tailoring glass compositions to meet specific application demands while maintaining durability and functionality.

Key advances in the development of glasses based on oxyfluorotellurite and TeO_2 have demonstrated their versatility as host matrices for various modifying agents, such as MoO_3 and BaO . These modifications significantly influence the density, connectivity, and radiation attenuation properties of the vitreous network. The addition of fluorides and oxides enables precise control of the structural and optical properties, ensuring improved shielding performance against gamma radiation and charged particles.

This chapter also reviews the role of these modifications in improving thermal stability, optical performance, and radiation shielding capabilities, based on recent findings (Alzahrani et al., 2021; Al-Buriahi et al., 2022; Gunha et al., 2022; Alzahrani et al., 2022; Gunha et al., 2023; Alfryyan et al., 2023; Gunha et al., 2024). A detailed discussion of these studies emphasizes the importance of understanding the interplay between structural characteristics and radiological protection efficiency.

In presenting an integrated analysis of the physical, thermal, optical and shielding properties, this chapter aims to guide future research and development in the design of advanced materials for radiological protection.

CHEMICAL COMPOSITION AND DENSITY

The chemical composition and density of the glasses are key factors that influence their effectiveness as radiation-shielding materials. The glasses investigated in this

study were synthesized using the melt-quenching method, a well-established technique for producing amorphous materials with customized physical and chemical properties. This method involves heating the precursors to their melting point and rapidly cooling them to prevent crystallization, thereby preserving the amorphous glass structure.

Table 6 summarizes the chemical compositions and densities of the synthesized glass samples, including $\text{TeO}_2\text{-Li}_2\text{O}$, $\text{TeO}_2\text{-Li}_2\text{O-BaO}$, and $\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$. These variations in composition provide a systematic approach to evaluating how different modifiers, such as BaO and MoO_3 , influence the structural, thermal, and radiation shielding properties of glasses.

Table 6 – Chemical Composition and Density of $\text{TeO}_2\text{-Li}_2\text{O-BaO}$ and $\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$ Glass Samples. The table presents the molar proportions of the main components (TeO_2 , Li_2O , BaO, and MoO_3) and the corresponding densities, highlighting how the incorporation of BaO and MoO_3 affects the glass properties.

Sample	Stoichiometry	TeO_2 (mol%)	Li_2O (mol%)	Other (mol%)	Density (g/cm^3)
TeLi-Mo1	$\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$	80	20	0 (MoO_3)	4.981
TeLi-Mo2	$\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$	70	25	5 (MoO_3)	4.746
TeLi-Mo3	$\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$	60	30	10 (MoO_3)	4.486
TeMo-Li1	$\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$	69	0	31 (MoO_3)	5.09
TeMo-Li2	$\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$	59	5	36 (MoO_3)	4.89
TeMo-Li3	$\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$	49	10	41 (MoO_3)	4.73
TeMo-Li4	$\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$	39	15	46 (MoO_3)	4.51
TLB05	$\text{TeO}_2\text{-Li}_2\text{O-BaO}$	75	20	5 (BaO)	4.936
TLB10	$\text{TeO}_2\text{-Li}_2\text{O-BaO}$	75	15	10 (BaO)	5.09
TLB15	$\text{TeO}_2\text{-Li}_2\text{O-BaO}$	75	10	15 (BaO)	5.23
TLB20	$\text{TeO}_2\text{-Li}_2\text{O-BaO}$	75	5	20 (BaO)	5.36
TLB25	$\text{TeO}_2\text{-Li}_2\text{O-BaO}$	75	0	25 (BaO)	5.36

Source: (Alzahrani et al., 2022; Alfryyan et al., 2023; Gunha et al., 2024).

In the study of $\text{TeO}_2\text{-Li}_2\text{O-BaO}$ glasses, the incorporation of BaO was found to increase the glass density, directly enhancing its gamma radiation and the absorption properties of charged particles. Specifically, the density increased from 4.93 g/cm^3 to 5.36 g/cm^3 as the BaO concentration increased from 5% to 25%. This increase in density corresponded to higher mass attenuation coefficients for gamma radiation, ranging from 0.0329 to $1.5964 \text{ cm}^2/\text{g}$. However, the neutron absorption capacity decreased with the addition of BaO, suggesting that while higher density benefits photon absorption, it does not have the same effect on neutrons (Alzahrani et al., 2022).

Similarly, the addition of MoO_3 was shown to enhance glass density, contributing to improved gamma radiation and charged particle attenuation. Glasses modified with MoO_3 also demonstrated notable improvements in structural and thermal properties, such as an increase in glass transition temperature (T_g) and higher thermal stability. These enhancements are attributed to the structural modifications caused by MoO_3 , including an increase in non-bridging oxygens (NBOs), which promotes greater interaction with radiation and improves shielding efficiency (Alfryyan et al., 2023; Gunha et al., 2024).

Analyzing the chemical composition alongside physical properties such as density

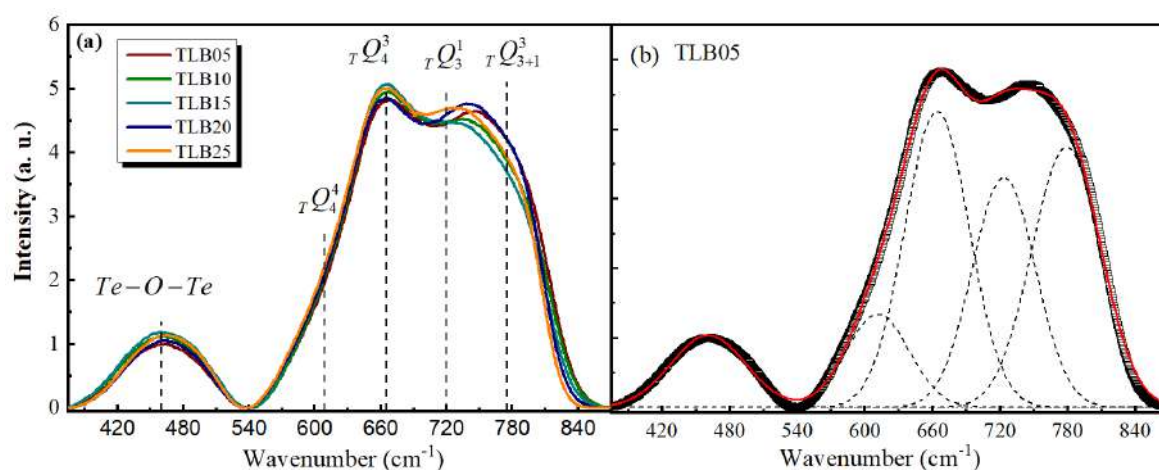
provides a comprehensive understanding of the relationship between the glass structure and its functionality as a shielding material. These findings highlight the importance of optimizing glass formulations to maximize their effectiveness in attenuating various types of radiation, which will be further discussed in the following sections of this chapter.

STRUCTURAL AND OPTICAL PROPERTIES

The structural properties of the glasses were analyzed using Raman and FTIR spectroscopy, which confirmed the presence of characteristic TeO_4 structural units, including Te-O-Te stretching and bending bands. These spectroscopic techniques revealed significant alterations in the glass network induced by the incorporation of MoO_3 and BaO. These modifications directly affected the network connectivity and increased the presence of non-bridging oxygens (NBOs), which play a crucial role in determining the glasses' properties.

Figure 49 illustrates the Raman spectrum for glasses modified with BaO, highlighting the structural changes introduced by varying BaO concentrations. Similarly, Figure 50 presents the Raman spectrum for the MoO_3 -modified glasses, showcasing the impact of MoO_3 on the glass structure and the resulting network reorganization.

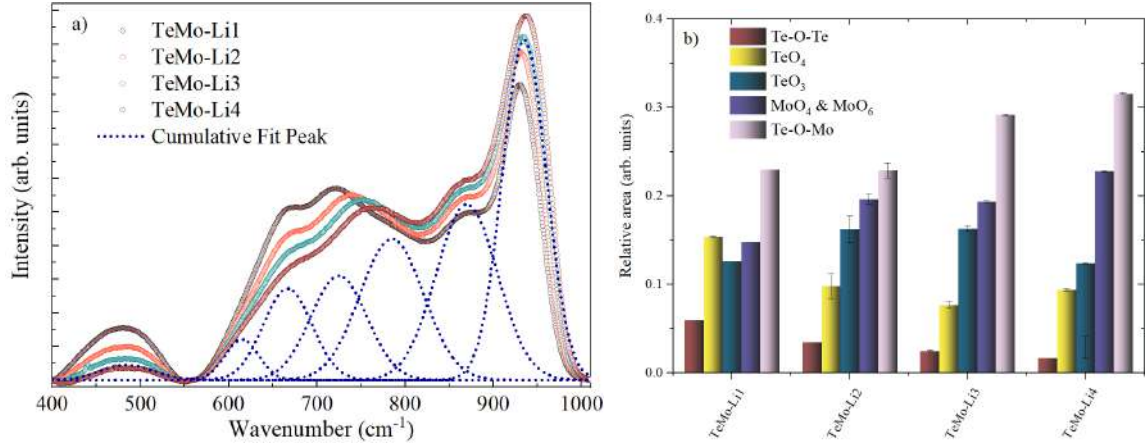
Figure 49 – (a) Raman spectra of all TeO_2 - Li_2O -BaO glass samples, highlighting the variations in band intensities associated with structural bonds as the BaO concentration increases. (b) Gaussian fitting of the five vibrational modes centered at 450, 611, 660, 730, and 780 cm^{-1} for the TLB05 sample, illustrating the decomposition of the Raman peaks.



Source: (Alzahrani et al., 2022).

The incorporation of BaO into the glass matrix modifies the network structure by partially substituting TeO_2 units, resulting in a rearrangement of structural components and an increase in the formation of non-bridging oxygens (NBOs). Raman spectroscopy revealed shifts in structural vibrations, characterized by the emergence of bands associated with Te-O-Ba bonds and a reduction in more stable TeO_4 units. These changes suggest a

Figure 50 – (a) Raman spectra of $\text{TeO}_2\text{-Li}_2\text{O-MoO}_3$ glass samples, showing variations in the intensities of bands associated with different structural bonds. (b) Deconvoluted areas corresponding to each Raman assignment mode, highlighting the contributions of structural units such as Te-O-Te , TeO_4 , TeO_3 , MoO_4 , and MoO_6 .



Source: (Gunha et al., 2024).

less ordered glass network, with an increase in NBO content and an altered connectivity (Alzahrani et al., 2022).

Similarly, the addition of MoO_3 introduces substantial structural changes by replacing TeO_4 units, creating a more dense and complex network. Raman spectra showed an increase in the frequency of asymmetric Te-O vibrations and the formation of Mo-O units, both indicative of higher NBO quantities. These modifications enhance the density and rigidity of the network, improving the mechanical properties and thermal stability. Furthermore, the presence of MoO_3 favors the reduction of TeO_4 units in exchange for TeO_3 and MoO_4 units, resulting in a more compact and thermally resistant structure. This densified network is essential to improve gamma radiation and charge particle absorption, making these glasses highly effective for radiological shielding applications (Alfryyan et al., 2023; Gunha et al., 2024).

In summary, the structural alterations induced by BaO and MoO_3 contribute to optimizing the mechanical, thermal, and radiological properties of the glass. These findings underscore the importance of controlling the chemical composition in the development of advanced vitreous materials with superior performance for radiological protection.

THERMAL PROPERTIES

The thermal properties of the glasses were evaluated using Differential Scanning Calorimetry (DSC), a technique that examines the impact of varying concentrations of MoO_3 and BaO on the thermal stability of the materials. The results demonstrated that both oxides positively influence the glass transition temperature (T_g) and the crystallization temperature (T_x), which are critical parameters for ensuring the durability and

performance of these glasses in high-radiation environments. Tables 7 and 8 summarize the thermal properties of glasses with BaO and MoO₃, respectively.

The addition of BaO to the glass matrix significantly increased both T_g and T_x , indicating improved thermal stability. As a heavy, high-density oxide, BaO reinforces the glass network, increasing rigidity and resistance to thermal deformation. A progressive increase in T_g and T_x with increasing concentration of BaO suggests improved resistance to heat-induced degradation, making these glasses particularly suitable for applications in environments with high temperatures and continuous exposure to radiation (Alzahrani et al., 2022).

Similarly, the incorporation of MoO₃ strengthened the glass network by introducing MoO₄ units, which partially replaced TeO₂. This substitution improved network connectivity, reduced atomic mobility, and delayed crystallization, resulting in higher crystallization temperatures (T_x) and crystallization peak (T_p) temperatures. Raman and FTIR analyses confirmed these structural modifications, highlighting the formation of a more complex and dense glass network that withstands higher temperatures without crystallizing. This enhanced stability is particularly advantageous for maintaining performance in environments of intense radiation where thermal resistance is essential (Alfryyan et al., 2023; Gunha et al., 2024).

The increased thermal stability provided by BaO and MoO₃ enhances the suitability of these glasses for use in high-radiation environments, such as nuclear reactors, radiation laboratories, and medical devices. Glasses with elevated values of the values of T_g and T_x are less prone to structural deformations caused by high temperatures, ensuring consistent and effective radiation shielding over time.

In conclusion, the incorporation of BaO and MoO₃ into the glass matrix not only improves its structural and optical properties but also significantly enhances the thermal stability. This robust thermal resistance ensures the longevity and reliability of these materials in demanding radiological protection applications.

Table 7 – Thermal Properties of TeO₂-Li₂O-BaO Glass Samples, Including Glass Transition Temperature (T_g), Crystallization Temperature (T_x), Crystallization Peak Temperature (T_p), and the Difference Between T_x and T_g (ΔT)

Saples (mol%)	T_g (°C)	T_x (°C)	T_p (°C)	ΔT (°C)
TLB05	261	340	387	79
TLB10	266	387	402	121
TLB15	277	394	415	117
TLB20	301	400	411	99
TLB25	325	369	396	44

Source: (Alzahrani et al., 2022).

Table 8 – Thermal Properties of TeO₂-Li₂O-MoO₃ Glass Samples, Including Glass Transition Temperature (T_g), Crystallization Temperature (T_x), Crystallization Peak Temperature (T_p), and the Difference Between T_x and T_g (ΔT)

Samples	T_g (°C)	T_x (°C)	T_p (°C)	ΔT (°C)
TeLi-Mo1	320	370	410	90
TeLi-Mo2	330	380	420	100
TeLi-Mo3	340	390	430	110

Source: (Alzahrani et al., 2022; Alfryyan et al., 2023; Gunha et al., 2024).

RADIATION SHIELDING PROPERTIES

The effectiveness of glasses in radiation shielding was assessed by calculating the mass attenuation coefficients (MAC), which quantitatively measure the ability of these materials to absorb and attenuate radiation. The results demonstrate that modification of the glasses with MoO₃ and BaO significantly enhances their radiation shielding capabilities, particularly for gamma radiation at low energies. This improvement is attributed to the increased density of the materials, which is directly linked to higher attenuation coefficients. These properties are critical for applications requiring efficient gamma radiation shielding, such as nuclear facilities and medical imaging systems.

Table 9 provides the mass attenuation coefficients for various photon energies, highlighting the superior performance of glasses modified with BaO and MoO₃. Furthermore, Table 10 presents the coefficients for fast neutron removal and thermal neutron absorption, showcasing the ability of these materials to interact with and reduce neutron flux.

By analyzing these coefficients, it becomes evident that the compositional adjustments achieved with BaO and MoO₃ not only enhance the density but also optimize the interaction of glasses with radiation, contributing to their overall effectiveness as shielding materials. These results emphasize the importance of tailoring chemical modifications to develop materials that meet specific demands for radiological protection in diverse applications.

Tables 11 and 12 present the cross sections of the fast neutron removal values for the glasses studied. In the TLB series, the cross-section ranges from 0.099 to 0.101 cm⁻¹ as the BaO concentration decreases from 25 to 5 mol%. Increasing the BaO content reduces the partial densities of Li, O, and Te, thereby reducing the glass's ability to remove fast neutrons. Despite this, TLB25 glass, with a cross-section of 0.0995 cm⁻¹, still outperforms ordinary concrete, which has a cross-section of 0.0957 cm⁻¹.

For TeLi-Mo glasses, the Σ_R values are 0.1032, 0.1013, and 0.0990 cm⁻¹ for TeLi-Mo1, TeLi-Mo2, and TeLi-Mo3, respectively. These results indicate a decline in neutron removal capacity with increasing MoO₃ content. The higher MoO₃ concentration reduces the partial density of oxygen and lowers the overall mass of the glass, weakening its scattering

Table 9 – Mass attenuation coefficients (cm^2/g) for different photon energies of glasses modified with BaO and MoO_3 , obtained through calculations using the XCOM software.

Sample	0.1 (MeV)	0.2 (MeV)	0.5 (MeV)	1.0 (MeV)	5.0 (MeV)	10.0 (MeV)
TeLi-Mo1	1.411	0.290	0.091	0.058	0.033	0.034
TeLi-Mo2	1.368	0.284	0.091	0.058	0.032	0.033
TeLi-Mo3	1.319	0.277	0.090	0.058	0.032	0.033
TeMo-Li1	1.348	0.281	0.091	0.058	0.033	0.034
TeMo-Li2	1.305	0.275	0.090	0.058	0.033	0.034
TeMo-Li3	1.255	0.268	0.090	0.058	0.033	0.034
TeMo-Li4	1.198	0.256	0.090	0.059	0.033	0.034
TLB05	1.440	0.295	0.091	0.058	0.033	0.034
TLB10	1.484	0.301	0.092	0.058	0.033	0.034
TLB15	1.524	0.307	0.092	0.058	0.033	0.035
TLB20	1.561	0.312	0.093	0.058	0.033	0.035
TLB25	1.595	0.317	0.093	0.059	0.034	0.036

Source: (Alzahrani et al., 2022; Alfryyan et al., 2023; Gunha et al., 2024).

Table 10 – Thermal neutron absorption coefficients and fast neutron removal coefficients (cm^{-1}) of the modified glasses, indicating their effectiveness in neutron radiation attenuation.

Samples	σ_{coh}	σ_{inc}	σ_{abs}	σ_{tot}	Removal Coefficient
TLB05	1.058	0.125	9.541	10.724	0.101
TLB10	1.097	0.098	7.525	8.721	0.100
TLB15	1.133	0.069	5.272	6.475	0.100
TLB20	1.168	0.037	2.791	3.997	0.099
TLB25	1.205	0.002	0.087	1.295	0.099

Source: (Alzahrani et al., 2022) .

efficiency for fast neutrons. However, TeLi-Mo1 glass demonstrates superior shielding capability compared to ordinary concrete, which has a cross-section of 0.0930 cm^{-1} .

Glasses with higher densities, such as those modified with MoO_3 and BaO, demonstrate significantly improved mass attenuation coefficients, particularly in the low-energy range (below 100 keV). This enhancement is attributed to the increased probability of interaction between gamma photons and the atoms in the denser glass network. Higher density promotes absorption mechanisms such as the photoelectric effect, which predominates at these energy levels. Figures 51 and 52 illustrate that glasses containing BaO and MoO_3 achieve higher attenuation coefficients compared to unmodified glasses, highlighting their effectiveness and superiority as gamma radiation shielding materials (Alzahrani et al., 2022).

The addition of MoO_3 enhances the shielding capacity of glasses by not only increasing the density, but also introducing structural modifications that intensify interactions with radiation. MoO_3 promotes the formation of Mo-O units within the glass network, increasing connectivity and reducing atomic mobility, thus improving the absorption of gamma radiation. These structural changes result in a denser and more complex

Table 11 – Fast neutron removal cross-section of elements contained in the synthesized TeO₂–Li₂O–MoO₃ glasses.

Glass code	Element	Σ_R/ρ (cm ² /g)	Fraction by weight, w_i	Partial density (g/cm ³), W_i	Σ_R (cm ⁻¹)
TeLi–Mo1	Li	0.0839	0.02077	0.1034	0.0086
	O	0.0405	0.21547	1.0732	0.0434
	Mo	0.0151	0.0127	0.0636	0.0010
	Te	0.0134	0.76376	3.8042	0.0511
				Σ_R	= 0.1031
Total Σ_R for glass ‘TeLi–Mo1’ = 0.1032 cm ⁻¹					
TeLi–Mo2	Li	0.0839	0.027	0.1319	0.0110
	O	0.0405	0.217	1.0344	0.0419
	Mo	0.0151	0.013	0.1824	0.0028
	Te	0.0134	0.715	3.397	0.0455
				Σ_R	= 0.1013
Total Σ_R for glass ‘TeLi–Mo2’ = 0.1013 cm ⁻¹					
TeLi–Mo3	Li	0.0839	0.035	0.1611	0.0135
	O	0.0405	0.228	1.0494	0.0425
	Mo	0.0151	0.082	0.3712	0.0056
	Te	0.0134	0.660	2.9628	0.0397
				Σ_R	= 0.0990
Total Σ_R for glass ‘TeLi–Mo3’ = 0.0990 cm ⁻¹					

Source: (Alfryyan et al., 2023) .

Table 12 – Fast neutron removal cross-section of elements contained in the prepared xBaO–(25-x)Li₂O–75TeO₂ (x = 5, 10, 15, 20, & 25 mol%) glass system.

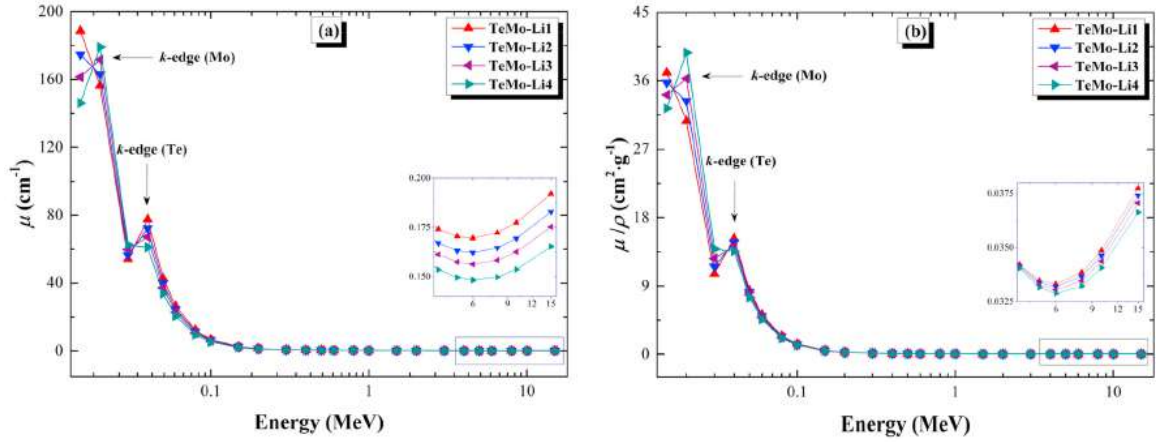
Element	Σ_R/ρ (cm ² /g)	TLB05 w_i	Partial ρ (g/cm ³)	Σ_R (cm ⁻¹)	TLB10 w_i	Partial ρ (g/cm ³)	Σ_R (cm ⁻¹)	TLB15 w_i	Partial ρ (g/cm ³)	Σ_R (cm ⁻¹)
Li	0.08399	0.02082	0.10278	0.00863	0.01493	0.07597	0.00638	0.00953	0.04983	0.00419
O	0.04053	0.20998	1.03645	0.04201	0.20069	1.02150	0.04140	0.19219	1.00513	0.04074
Te	0.01341	0.71770	3.54257	0.04750	0.68595	3.49147	0.04681	0.65668	3.43550	0.04606
Ba	0.01286	0.01550	0.25420	0.00327	0.02032	0.09844	0.00126	0.04064	0.11410	0.00591
Total				0.10141			0.10104			0.10049
Element	Σ_R/ρ (cm ² /g)	TLB20 w_i	Partial ρ (g/cm ³)	Σ_R (cm ⁻¹)	TLB25 w_i	Partial ρ (g/cm ³)	Σ_R (cm ⁻¹)			
Li	0.08399	0.00457	0.02450	0.00206	0.00000	0.00000	0.00000			
O	0.04053	0.18437	0.98324	0.04005	0.17717	0.97445	0.03949			
Te	0.01341	0.63018	3.37777	0.04529	0.60557	3.33061	0.04466			
Ba	0.01286	0.18087	0.96949	0.01247	0.21726	1.19494	0.01522			
Total				0.09987			0.09951			

Source: (Alzahrani et al., 2022) .

network, making the glasses particularly effective at attenuating low- to medium-energy photons. This makes MoO₃-modified glasses highly suitable for applications requiring minimized radiation penetration, such as medical devices, radiation laboratories, and other safety-critical environments (Alfryyan et al., 2023; Gunha et al., 2024).

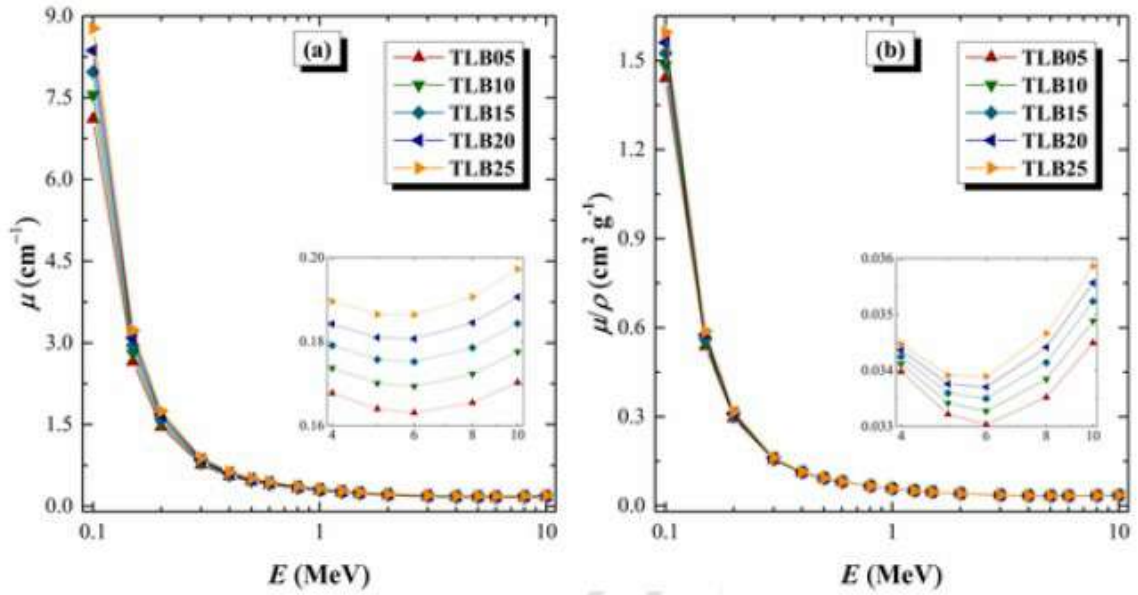
Although BaO improves photoelectric interactions due to its high atomic number, MoO₃ offers a balance between increased density and structural network modification, enabling efficient absorption of both photons and neutrons. Glasses containing MoO₃ exhibit a more balanced performance in gamma radiation and neutron absorption compared to glasses containing BaO alone, which are less effective for neutrons. Compared to conven-

Figure 51 – Variations of the attenuation coefficients for the synthesized $\text{TeO}_2\text{-MoO}_3\text{-Li}_2\text{O}$ glasses: (a) Linear attenuation coefficient and (b) Mass attenuation coefficient.



Source: (Gunha et al., 2024).

Figure 52 – Variations of the (a) linear attenuation coefficient and (b) mass attenuation coefficient as a function of photon energy in the prepared TLB glass system.



Source: (Alzahrani et al., 2022).

tional shielding materials, such as concrete and lead glasses, glasses modified with MoO_3 and BaO stand out for their tunable absorption properties, superior thermal stability, and lower environmental toxicity (Alzahrani et al., 2022).

CORRELATION BETWEEN STRUCTURAL COMPOSITION AND RADIATION SHIELDING EFFICIENCY

The relationship between the structure of glasses and their radiation absorption properties is critical to understanding their effectiveness as shielding materials. The structure of the glass network, the density of the material and the presence of specific elements such as BaO and MoO₃ are key factors influencing the radiation absorption capacity.

Incorporation of structural units such as MoO₄ and MoO₆ into MoO₃-modified glasses increases the complexity and connectivity of the glass network, resulting in a denser structure with improved radiation absorption properties. Raman spectra confirm the presence of these structural units, which are fundamental to improving shielding efficiency (Gunha et al., 2024; Alfryyan et al., 2023). The transition from TeO₄ to MoO₆ units not only boosts density but also optimizes shielding performance, particularly against gamma radiation and fast neutrons.

The density plays a crucial role in the radiation absorption capacity of glasses. MoO₃ modified glasses exhibit higher densities compared to BaO-containing glasses, leading to increased mass attenuation coefficients and greater effectiveness in absorbing gamma rays and neutrons (Alzahrani et al., 2022). In contrast, BaO-containing glasses are highly efficient at absorbing gamma radiation because of their high density and high atomic number of barium, which enhances interactions such as the photoelectric effect. However, their effectiveness is limited for neutron absorption, particularly for fast neutrons.

The presence of elements such as molybdenum (Mo) and barium (Ba) significantly influences the radiation properties of glasses. Molybdenum, with its high neutron absorption cross-section, makes MoO₃-modified glasses especially effective at shielding against thermal and fast neutron radiation. The results indicate that MoO₃-containing glasses outperform BaO-modified glasses in neutron absorption, while BaO glasses excel in photon absorption (Alfryyan et al., 2023; Gunha et al., 2024).

Compared to traditional shielding materials such as concrete and lead glasses, TeO₂-Li₂O-BaO-based compositions demonstrate superior photon attenuation due to their high density and the inclusion of barium. However, these glasses have limitations in neutron absorption. In contrast, MoO₃ modified glasses provide a more balanced performance for photon and neutron shielding, positioning them as versatile alternatives for radiological protection in environments with multiple radiation sources (Alfryyan et al., 2023; Gunha et al., 2024).

CONCLUSIONS

$\text{TeO}_2\text{-Li}_2\text{O-BaO}$ -based glasses and those modified with MoO_3 demonstrate promising radiation shielding properties. The introduction of BaO significantly enhances photon absorption, making these glasses highly effective for gamma radiation protection, particularly at low and medium energies. However, increasing the concentration of BaO reduces the capacity to absorb thermal and fast neutrons, as shown by the low fast neutron removal coefficients and thermal neutron absorption cross sections observed in the presence of a higher BaO content (Alzahrani et al., 2022).

In contrast, MoO_3 -modified glasses offer a more balanced combination of properties, enhancing the absorption of both photons and neutrons. This is due to the increased density and the formation of structural units such as MoO_4 , which improve the connectivity of the glass network and provide a larger neutron cross-section, thus optimizing shielding efficiency against neutron and gamma radiation (Alfryyan et al., 2023; Gunha et al., 2024).

Although BaO-containing glasses excel in gamma radiation absorption, they are less effective against fast neutrons due to barium's lower interaction with neutron particles. In comparison, MoO_3 -modified glasses show good overall performance but still face challenges in optimizing fast neutron absorption.

Therefore, chapter 4 will focus on exploring new compositions and structural adjustments to overcome these limitations, with the aim of developing materials that offer an optimal balance of photon and neutron absorption properties for use in diverse radiological environments. Ongoing research will continue to investigate the combination of various oxides and network modifications to create shielding glasses that provide superior performance where previous compositions have fallen short.

Figure 53 presents the results for the 65TZMo and 60TZMo samples, as an example. The homogeneity on the surface can be observed, and this characteristic remains constant throughout the sample. The presence of a smooth surface free from any crystalline formation is evident, which is fully corroborating the XRD results, which indicated the absence of crystalline phases. The other samples showed similar behavior.

Figure 54 – **SEM** The micrograph of the sample surface is as follows: **(a)** 65TZLi e **(a)** 60TZLi, at 1.000 kx magnification.

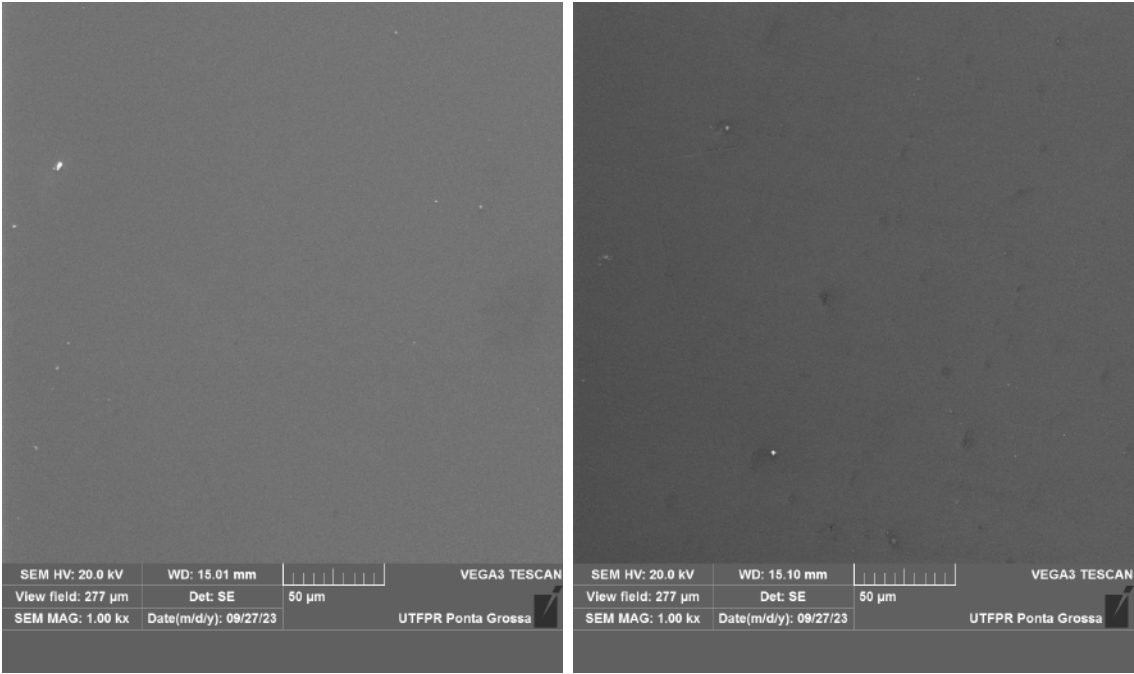


Figure 55 – **SEM** The micrograph of the sample surface is as follows: **(a)** 65TZNa e **(a)** 60TZNa, at 1.000 kx magnification.

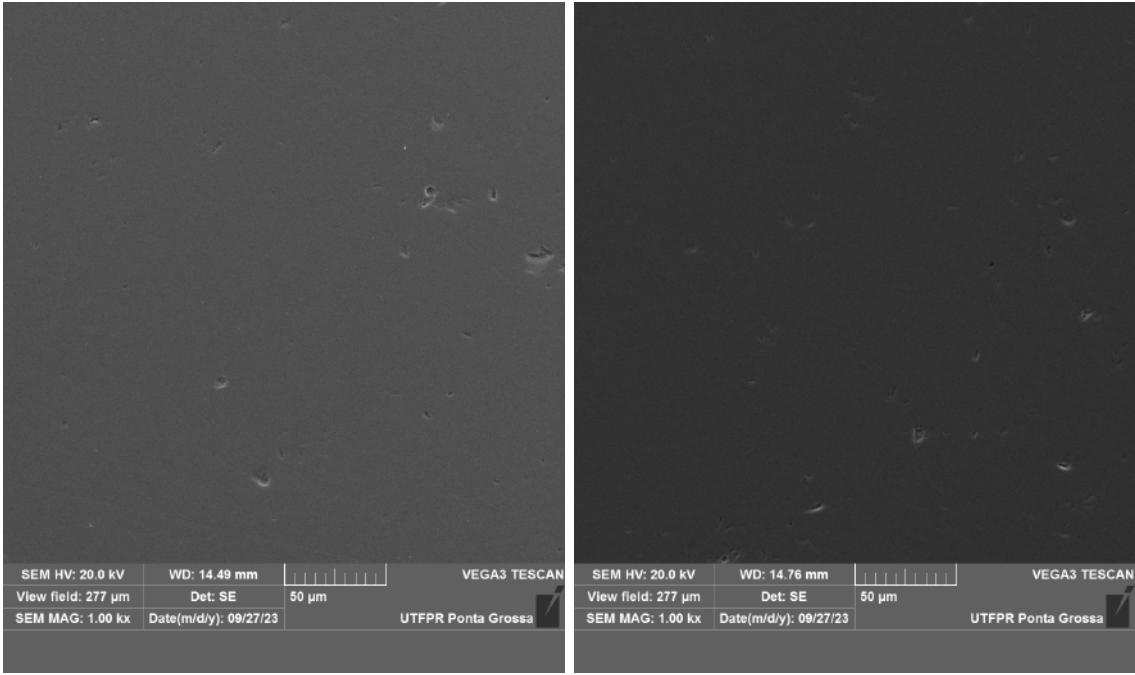


Figure 56 – **SEM** The micrograph of the sample surface is as follows: (a) 65TZTi e (a) 60TZTi, at 1.000 kx magnification.

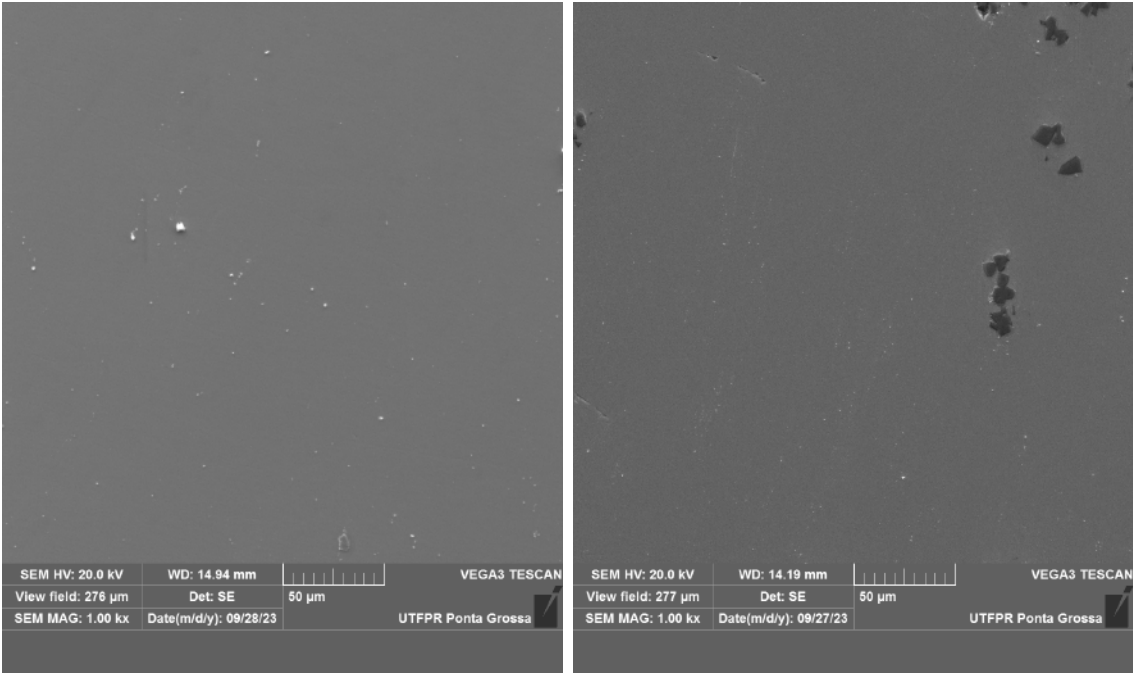
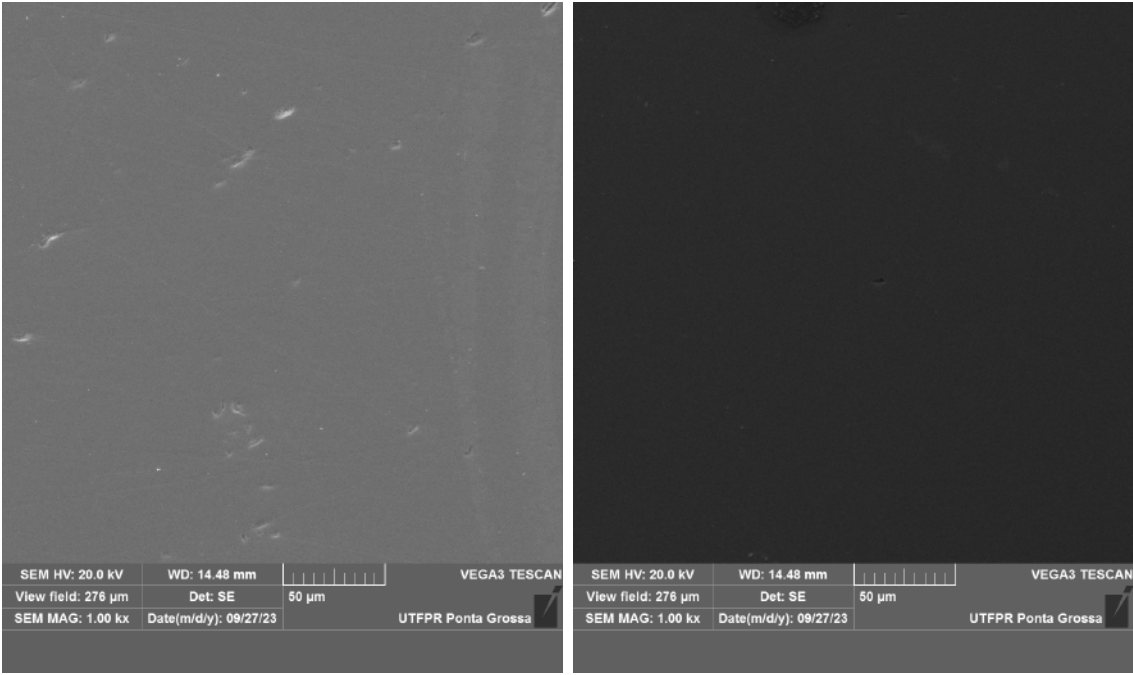


Figure 57 – **SEM** The micrograph of the sample surface is as follows: (a) 65TLBa e (a) 60TZBa, at 1.000 kx magnification.



ELEMENTAL AND SPECTRAL MAPS OF THE SAMPLES

Figure 58 – EDS Spectral map and color mapping obtained by EDS for a sample of 65TZLi.

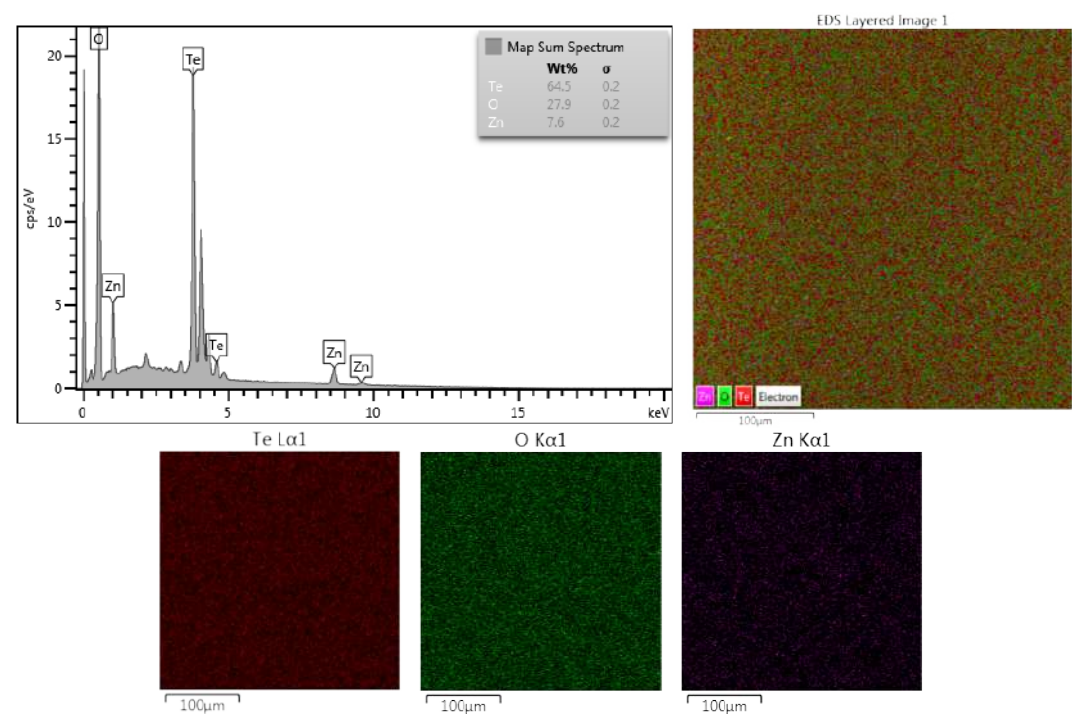


Figure 59 – EDS Spectral map and color mapping obtained by EDS for a sample of 65TZNa.

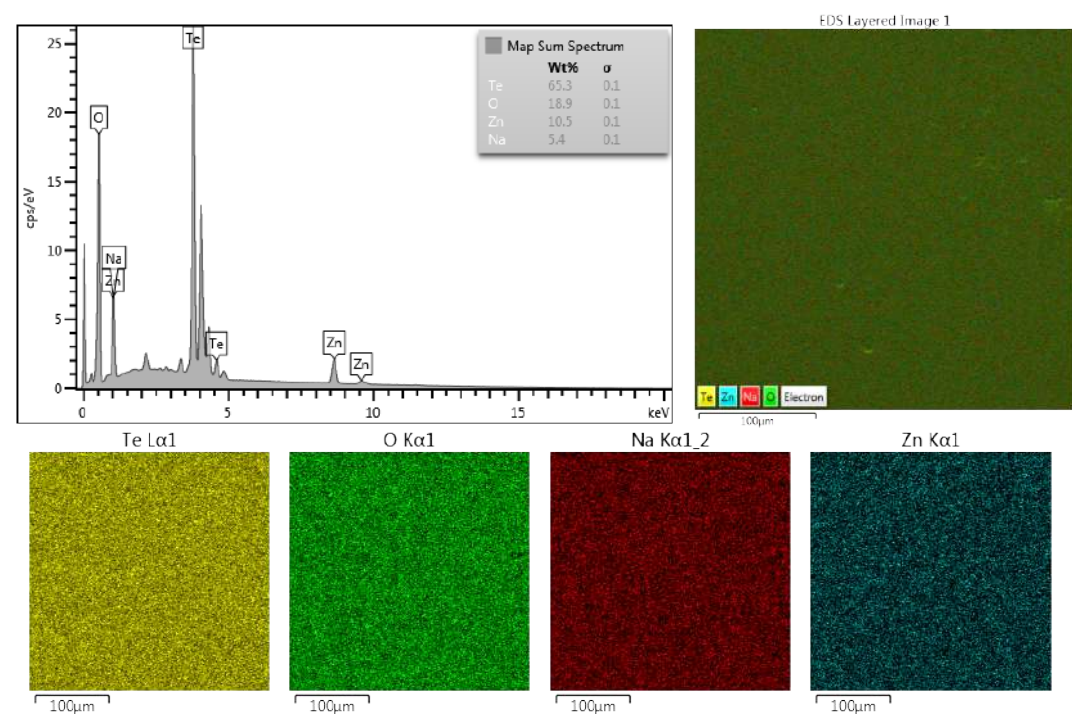


Figure 60 – Spectral map and color mapping obtained by EDS for a sample of 65TZTi.

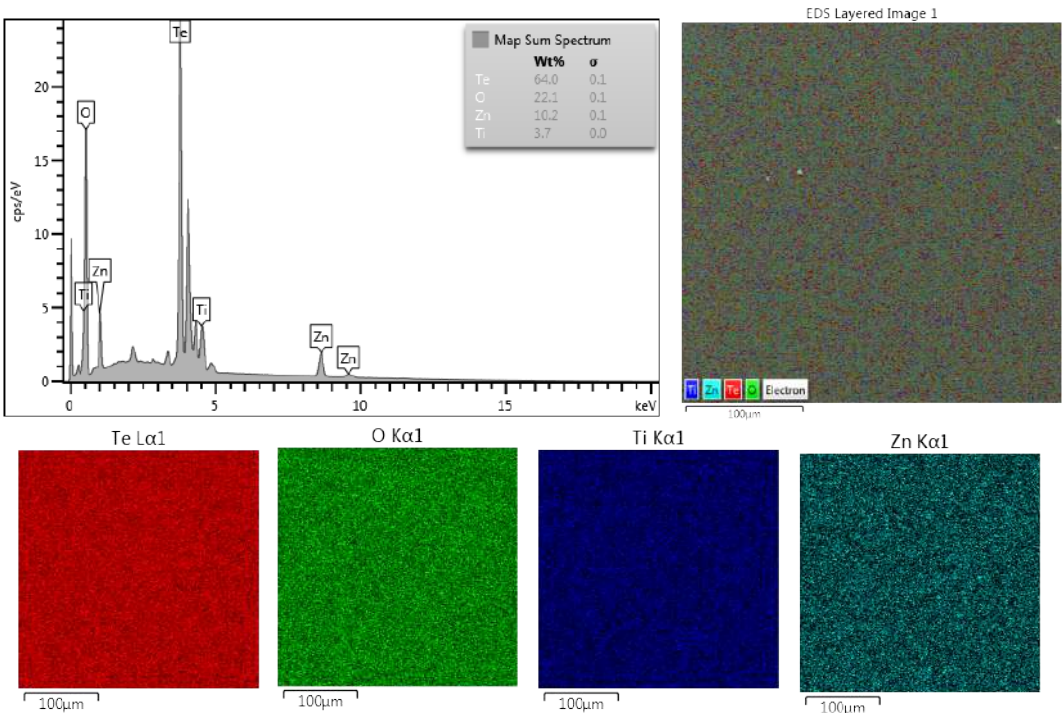


Figure 61 – EDS Spectral map and color mapping obtained by EDS for a sample of 65TZBa.

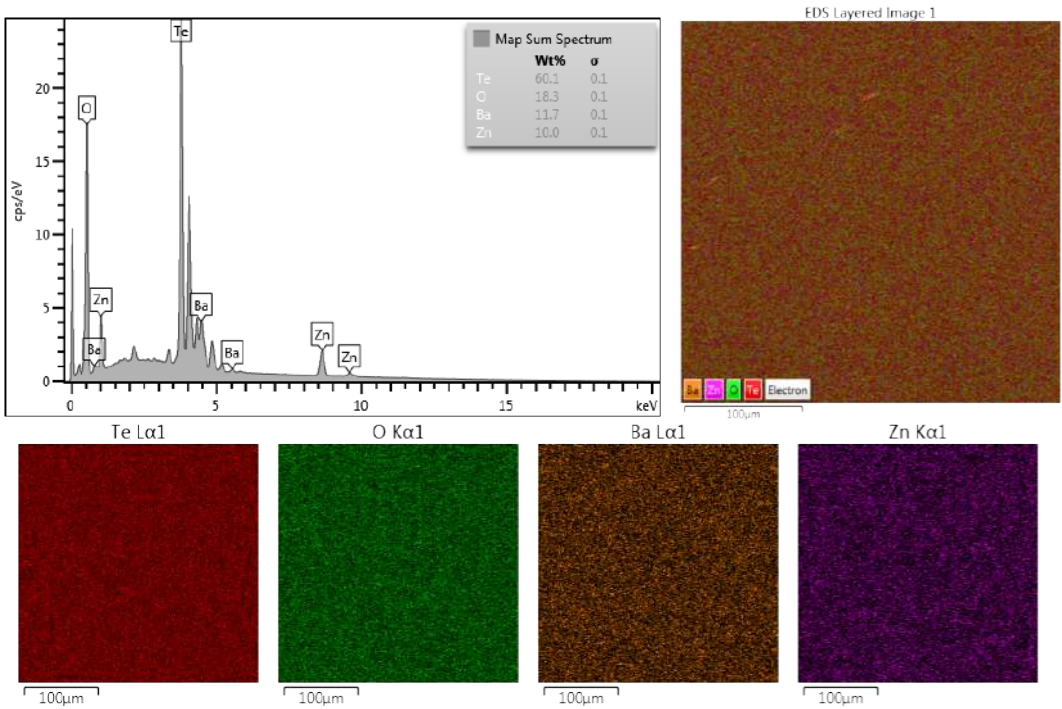


Figure 62 – EDS Spectral map and color mapping obtained by EDS for a sample of 60TZLi.

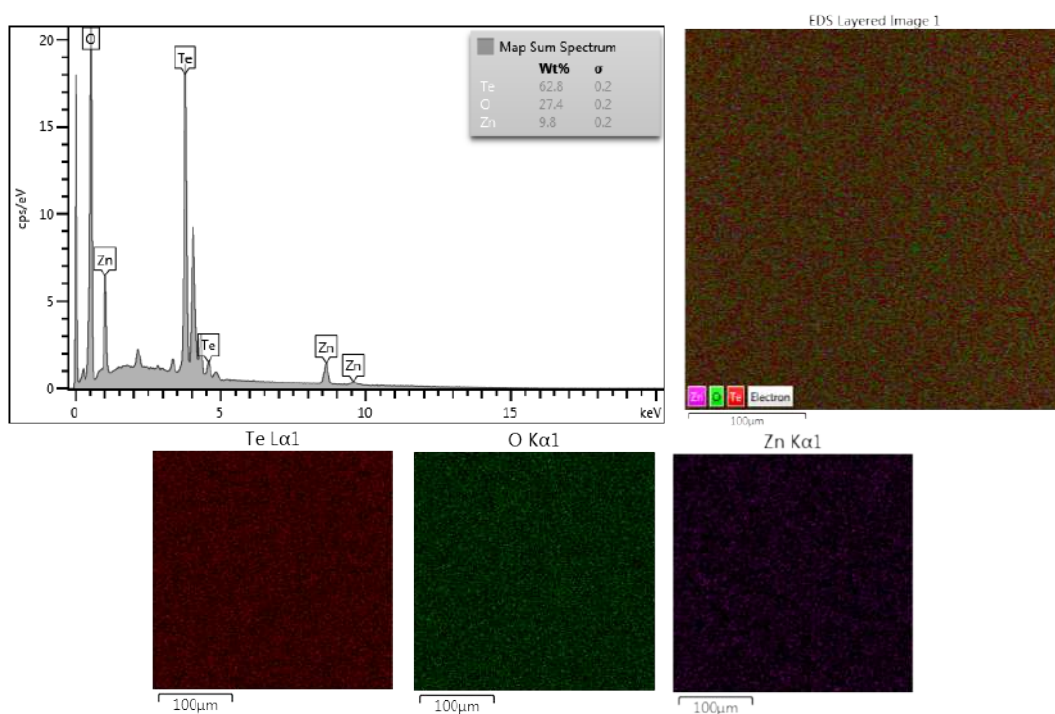


Figure 63 – EDS Spectral map and color mapping obtained by EDS for a sample of 60TZNa.

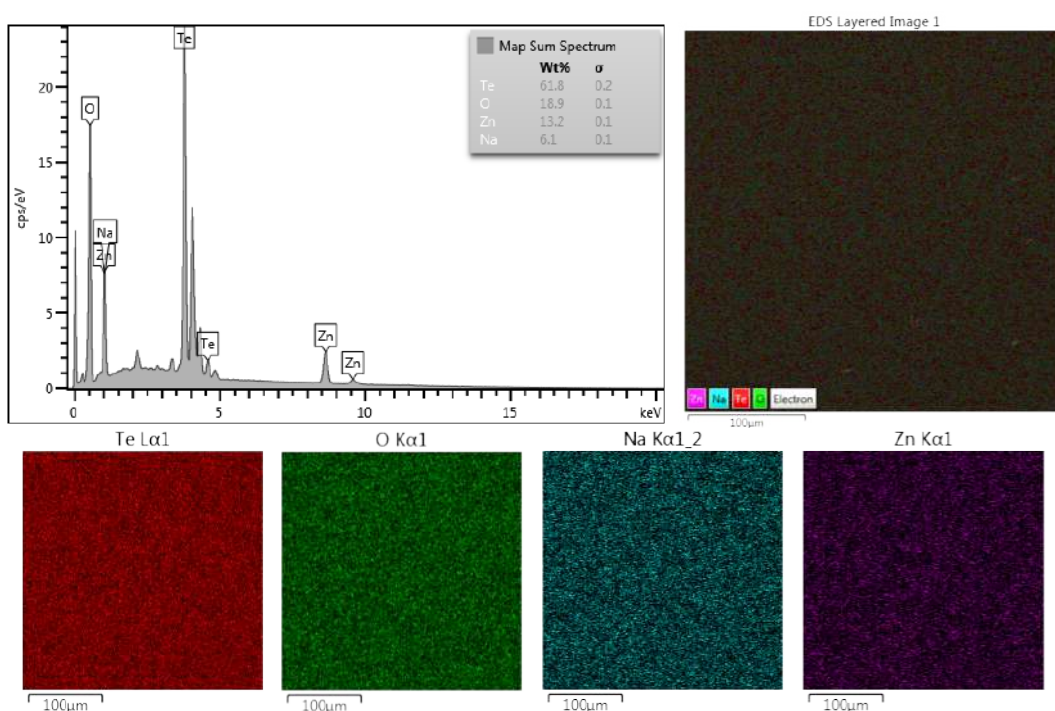


Figure 64 – EDS Spectral map and color mapping obtained by EDS for a sample of 60TZTi.

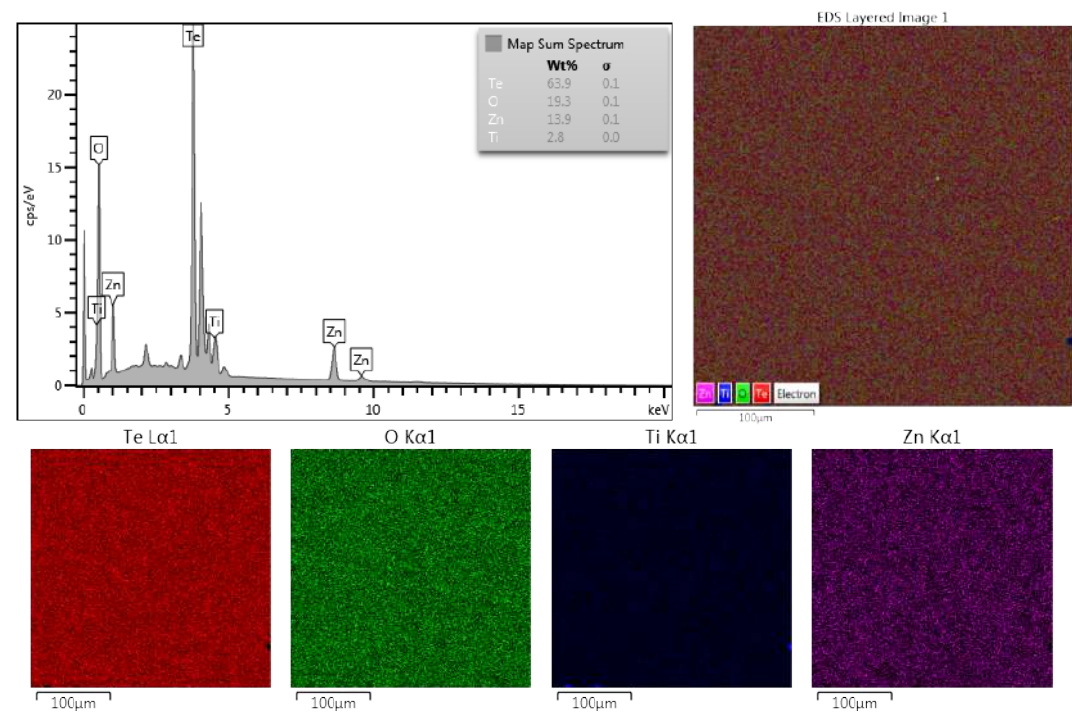


Figure 65 – EDS Spectral map and color mapping obtained by EDS for a sample of 60TZMo.

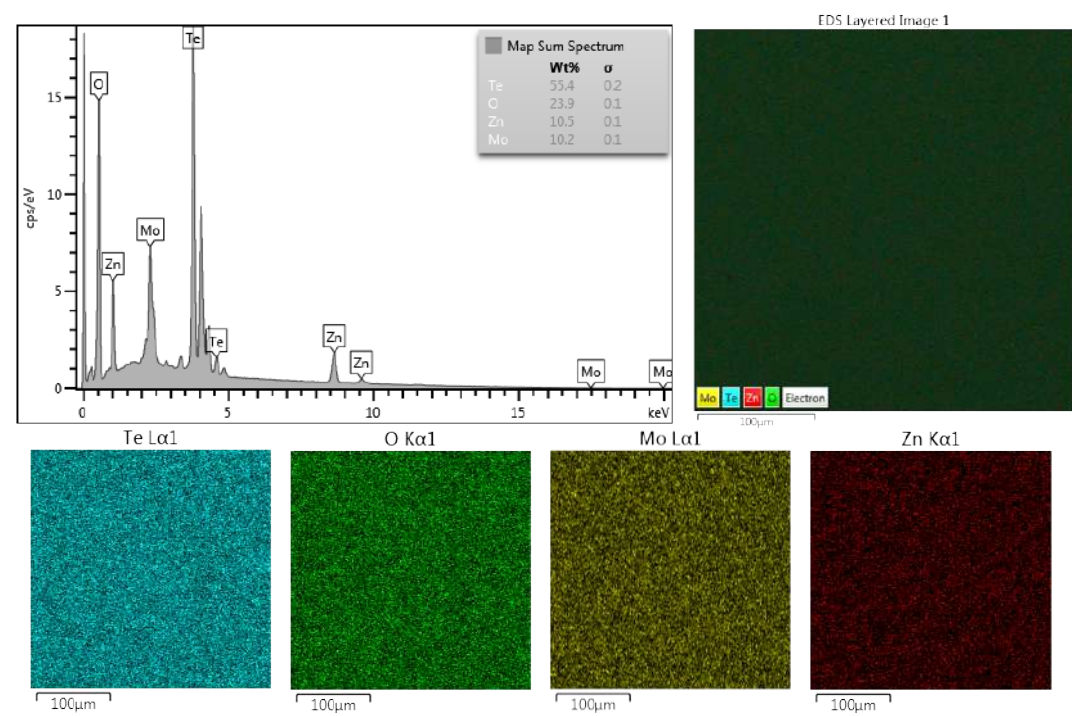
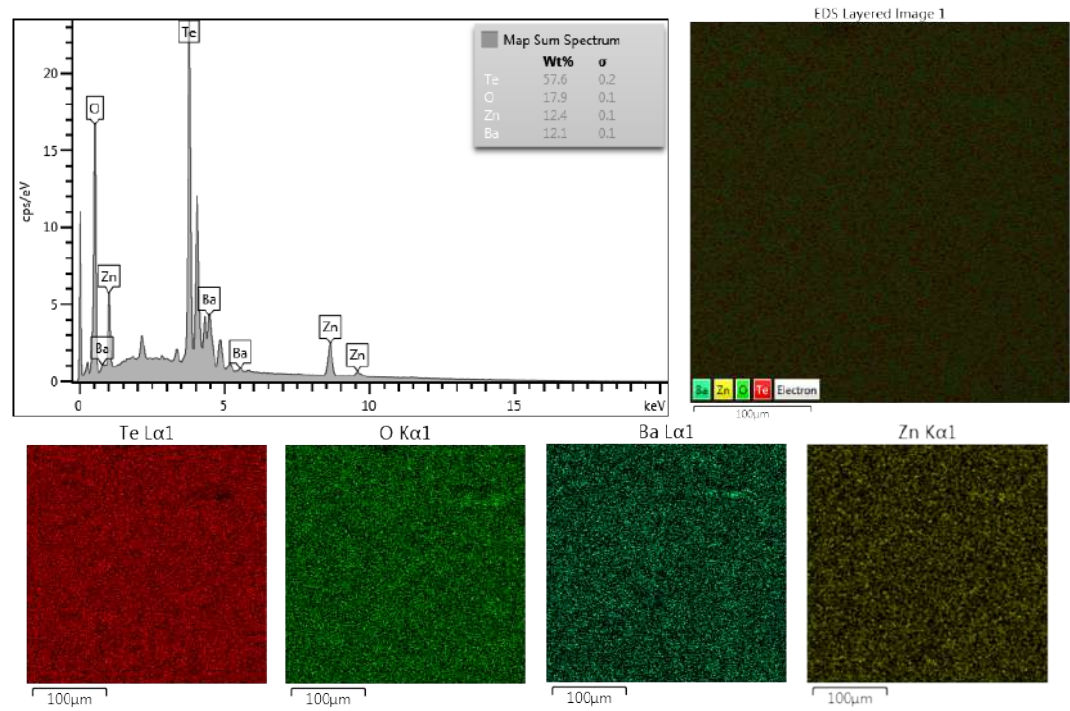


Figure 66 – **EDS** Spectral map and color mapping obtained by EDS for a sample of 60TZBa.



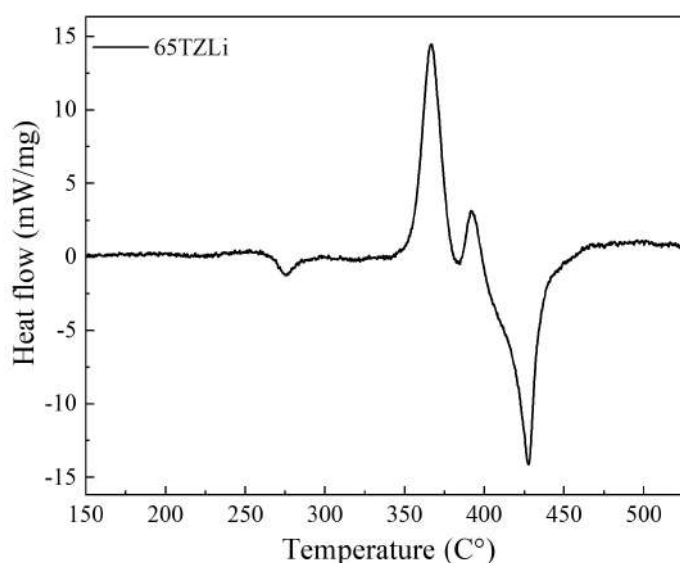
DSC CURVE

The DSC curve for the 65TZLi sample, shown in Figure 67, provides a detailed view of the thermal transitions characteristic of this glass composition. Two distinct transitions are observed: a first-order transition, represented by an asymmetric exothermic peak, and a second-order transition, marked by a change in the baseline. These transitions are critical for determining key thermal parameters such as the glass transition temperature (T_g), the initial crystallization temperature (T_x), the thermal stability parameter (ΔT) and the exothermic crystallization peak (T_p).

The glass transition temperature (T_g) is identified at the intersection of the baseline tangent with the tangent at the inflection point of the first endothermic peak. This parameter marks the temperature at which the glass transitions from a liquid-like amorphous state to a more rigid structure. The onset crystallization temperature (T_x) is determined at the intersection of the baseline tangent with the tangent at the inflection point of the first exothermic peak. It represents the temperature at which the glass begins to crystallize, transitioning to a crystalline phase. Finally, the exothermic crystallization peak (T_p) corresponds to the highest point of the first exothermic peak, indicating the maximum rate of heat release during the crystallization process.

These parameters, obtained from the DSC curve, are essential for understanding the thermal stability and resistance of the glass to crystallization. The analysis provides insights into how different modifying oxides influence the rigidity, compactness, and thermal behavior of the glass network, making it a fundamental tool in the characterizing of tellurite glasses.

Figure 67 – DSC curve for the 65TZLi sample, illustrating the characteristic thermal transitions used to determine T_g , T_x , and T_p .



OPTICAL ABSORPTION

Figure 68 – Plots of $(\alpha \cdot h\nu)^m$ versus photon energy for indirect electronic transitions in alkali-containing group 60.

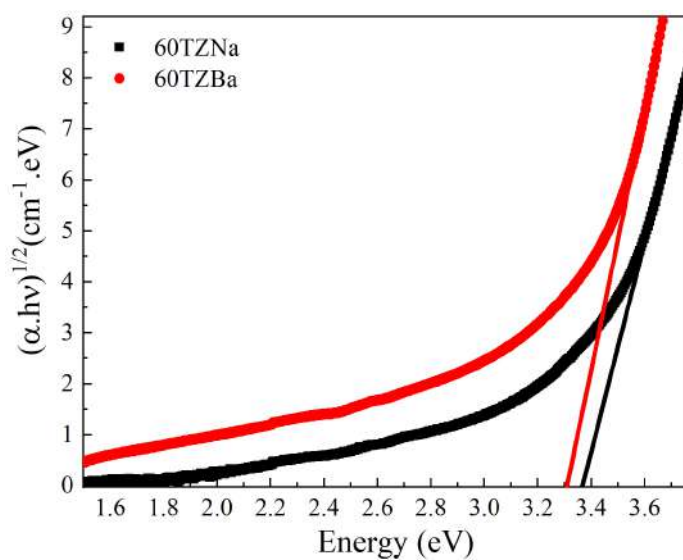
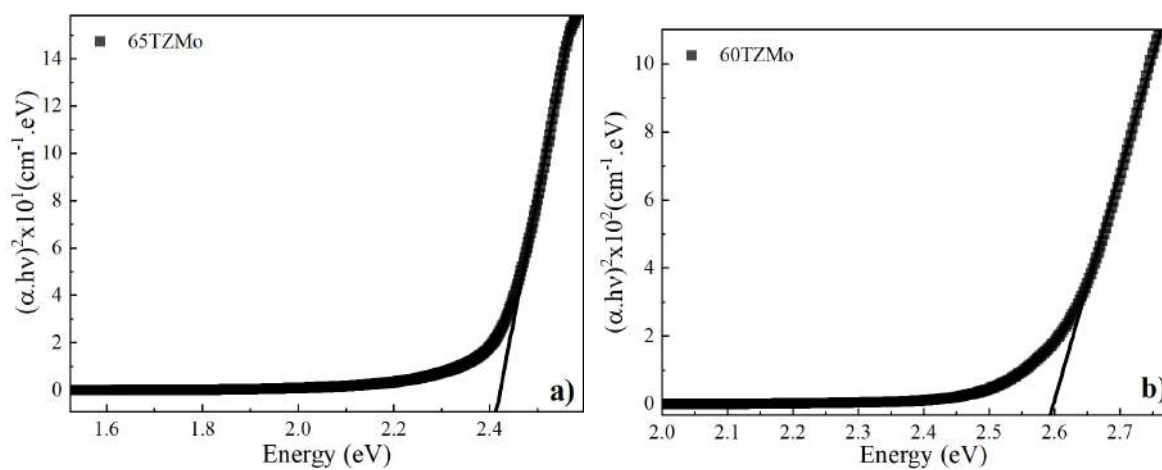


Figure 69 – Plots of $(\alpha \cdot h\nu)^m$ versus photon energy for direct electronic transitions in molybdenum-containing: a) Group 65. b) Group 60.

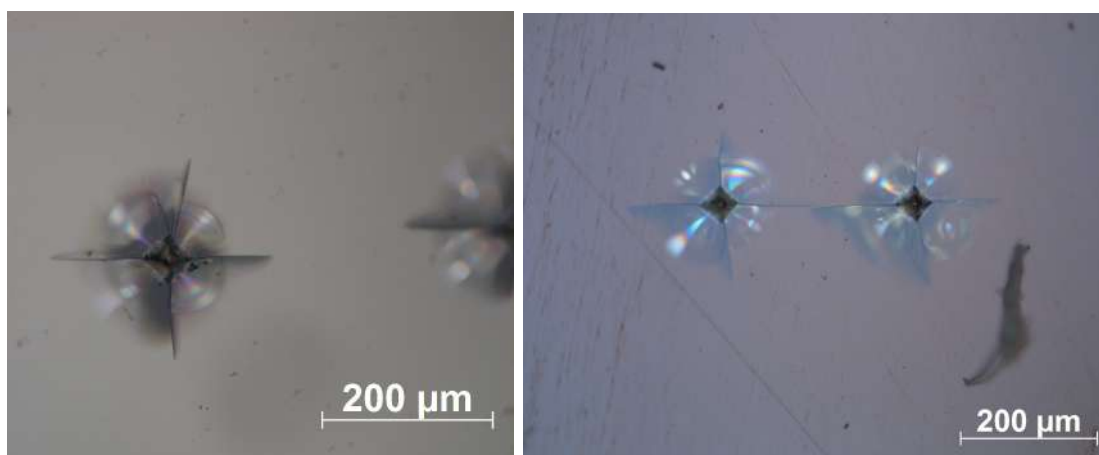


OPTICAL MICROSCOPY

Optical microscopy (OM) is a technique that is used to examine the microstructural characteristics of materials with high resolution. For the tellurite glass samples, OM was employed to provide a detailed visualization of the surface, allowing the identification of microcracks and other structural imperfections.

Figures 70 a and b show the optical microscopy images of the 60TZBa and 65TZMo samples, respectively. These images reveal a relatively smooth and homogeneous surface, with no significant crystalline formations or phase separations, confirming the amorphous nature of the glasses. The absence of such crystalline phases aligns with the XRD results, which also indicated a lack of crystallinity in these samples.

Figure 70 – **a)** Optical microscopy image of 60TZBa. **b)** Optical microscopy image of 65TZMo.



The images obtained by OM show a smooth and uniform surface, as observed in these samples, suggesting a well-prepared glass matrix with minimal structural defects. The 60TZBa sample, which contains BaO as a modifier, reveals a highly uniform texture with no visible imperfections. This homogeneity suggests that BaO contributes to the stability and uniformity of the glass matrix, enhancing its resistance to mechanical deformation and improving its optical transparency.

In contrast, the 65TZMo sample, modified with molybdenum oxide (MoO_3), exhibits an equally smooth surface, but with subtle variations in texture that may indicate slight differences in local structural organization. These variations could result from the dual role of MoO_3 as both a former and a modifier of the network, introducing a certain degree of microstructural heterogeneity that may affect the distribution of NBOs within the glass network, influencing its mechanical and optical properties.

Overall, OM provides valuable insights into the microstructure and quality of the glass samples. By confirming the absence of large-scale structural defects and highlighting subtle differences in morphology, OM helps to understand the impact of different modifiers on the glass matrix. For example, the inclusion of BaO appears to promote a stable and

defect-free surface, while MoO_3 introduces minor heterogeneities that could affect the performance of the materials under specific conditions (Yasaka et al., 2018).

Moreover, OM corroborates the results obtained from XRD. Although X-ray diffraction (XRD) provides information about the amorphous or crystalline nature of the materials, OM allows direct observation of surface features, offering a more comprehensive understanding of the quality and potential performance of the materials.

APPENDIX E – ACADEMIC BACKGROUND

I. Work related to the thesis

High thermal stability molybdenum-Boosted lithium tellurite glass for radiation shielding.; **Jaqueline Valeski Gunha**, Maryam Al Huwayz, Islam M. Nabil, Z.A. Alrowaili, M.S. Al-Buriahi, Andressa Novatski, Robson Ferrari Muniz: **Ceramics International** <https://doi.org/10.1016/j.ceramint.2024.07.271> (2024) (Gunha et al., 2024).

The effect of fluorine replacement on the physical properties of oxyfluorotellurite glasses TeO_2 - Li_2O - ZnO - ZnF_2 .; **Jaqueline Valeski Gunha**, Robson Ferrari Muniz, Aloisi Somer, Simone do R.F. Sabino, Daniele Toniolo Dias, R. El-Mallawany, Andressa Novatski: <https://doi.org/10.1016/j.jnoncrysol.2022.122083> **Journal of Non-Crystalline Solids** (2023) (Gunha et al., 2023).

Design, synthesis, and characterization of Pb-free tellurite glasses for radiation shielding applications. Nada Alfryyan, Z.A. Alrowaili, Robson Ferrari Muniz, Zainab Mufarreah Elqahtani, **Jaqueline Valeski Gunha**, Andressa Novatski, João Luiz Gomes Junior, Francisco Carlos Serbena, I.O. Olarinoye, M.S. Al-Buriahi. **Radiation Physics and Chemistry**. (2023) <https://doi.org/10.1016/j.radphyschem.2023.110969> (Alfryyan et al., 2023).

A synergistic effect of heavy metal oxides to enhance the physical, optical, and radiation-absorption properties of TeO_2 - Li_2O - BaO glasses. Jamila S. Alzahrani, Robson Ferrari Muniz, Z.A. Alrowaili, Andressa Novatski, **Jaqueline Valeski Gunha**, Anderson Gonçalves, I.O. Olarinoye, M.S. Al-Buriahi. <https://doi.org/10.1016/j.ijleo.2022.169189> **Optik**. (2022) (Alzahrani et al., 2022).

Characterization of oxyfluorotellurite glasses with TeO_2 - Li_2O - ZnO - LiF composition.; **Jaqueline Valeski Gunha**, Robson Ferrari Muniz, Aloisi Somer, Anderson Gonçalves, Rafael Denkiewicz, Giulia de Souza Antero, Tasso O. Sales, Carlos Jacinto, Raouf El-Mallawany, Andressa Novatski. <https://doi.org/10.1016/j.ceramint.2021.10.224> **Ceramics International**. (2022) (Gunha et al., 2022).

II. Other works

Spectroscopic studies of TeO_2 -based glasses doped with Sm^{3+} ions and its use as an optical temperature sensor.; **Jaqueline Valeski Gunha**, Tasso O. Sales, Robson Ferrari Muniz, Wagner F. Silva, Aloisi Somer, Carlos Jacinto, Daniele Toniolo Dias, R El-Mallawany, Nelson Astrath and Andressa Novatski. <https://doi.org/10.1088/1402-4896/ad2a2c>. **Physica Scripta**. (2024) (Gunha et al., 2024b).

Influence of Sm_2O_3 ion concentration on physical and thermal properties, and Raman gain coefficient of TeO_2 - Li_2O - ZnO vitreous system.; **Jaqueline Valeski Gunha**,

Robson Ferrari Muniz, Aloisi Somer, Tasso de Oliveira Sales, Wagner Ferreira da Silva, Daniele Toniolo Dias, R. El-Mallawany, Carlos Jacinto da Silva, Nelson Guilherme Castelli Astrath, and Andressa Novatski. <https://doi.org/10.1007/s10854-023-11895-5>. **J Mater Sci: Mater Electron.** (2024) (Gunha et al., 2024a).

Down-and up-conversion processes in Nd^{3+}/Yb^{3+} co-doped sodium calcium silicate glasses with concomitant Yb^{2+} assessment.; Muniz, R. F., Zanuto, V. S., Gibin, M. S., **Gunha, J. V.**, Novatski, A., Rohling, J. H., Medina, A. N., Baesso, M. L. **Journal of Rare Earths.** (2022) <https://doi.org/10.1016/j.jre.2022.01.020> (Muniz et al., 2023).

Raman and photoacoustic spectroscopies of SnO_2 thin films deposited by spin coating technique.; Regiane Gordia Drabeski, **Jaqueline Valeski Gunha**, Andressa Novatski, Gelson Biscaia de Souza, Sergio Mazurek Tebcherani, Evaldo Toniolo Kubaski, Daniele Toniolo Dias. <https://doi.org/10.1016/j.vibspec.2020.103094> **Vibrational Spectroscopy.** (2020) (Drabeski et al., 2020).