IMPACT OF TITANIUM NITRIDE NANOPARTICLES ON STRUCTURE & OPTICAL PROPERTIES OF NEODYMIUM/THULIUM IONS CO-DOPED TELLURITE GLASS

NUR FARAH ASYIQA BINTI ABU ZAIBIDIN

UNIVERSITI SAINS MALAYSIA

2025

IMPACT OF TITANIUM NITRIDE NANOPARTICLES ON STRUCTURE & OPTICAL PROPERTIES OF NEODYMIUM/THULIUM IONS CO-DOPED TELLURITE GLASS

by

NUR FARAH ASYIQA BINTI ABU ZAIBIDIN

Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

September 2025

ACKNOWLEDGEMENT

This thesis would not have been possible without the continuous supervision, guidance, and support of my knowledgeable supervisor, Dr. Nur Nabihah binti Yusof, throughout its completion. I have gained valuable experimental skills, working with versatile instruments beyond my theoretical undergraduate experience. I am also grateful to the lab officers in the NOR Lab and other facilities where I conducted sample characterisation. Additionally, I sincerely appreciate Universiti Sains Malaysia for funding my research through the Short-Term Grant (Project No: 304/PFIZIK/6315739) and the Institute of Postgraduate Studies for awarding me the GRA Assist, alleviating my financial concerns regarding tuition fees.

Next, I would like to thank my father, Abu Zaibidin bin Abu Bakar, for his unwavering financial support throughout this project. Surely, I will repay you someday. I also appreciate your understanding of my struggles and hardships. My goal is not to make you all proud, but rather to pursue what I truly enjoy. Yet, I cannot say that I am proud or satisfied with what I have done and achieved over the past years.

Throughout this lonely and challenging journey, my sanity might not have remained intact, though I do have my moments of rage, if not for these people who showed up like angels. I would like to thank Maira for your kindness; Ajim for your emergency assistance; and that one online figure for your prayers and support. To my significant other, Muhamad Ezkil bin Uzair, I am deeply grateful for your unwavering emotional support, patience, advice, thoughts, strength, and willingness to stand by me even when I was at my most frustrating. Lastly, I thank my cowardly self for not giving up. For the love of physics and the unknown—into entropy we go.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

LIST OF ABBREVIATIONS

Ag	Silver
Au	Gold
Bi_2O_3	Bismuth Oxide
BO	Bridging Oxygen
Cu	Copper
FTIR	Fourier Transform Infrared
HR-TEM	High Resolution - Transmission Electron Microscope
JO	Judd-Ofelt
LSPR	Local Surface Plasmon Resonance
MIR	Mid-Infrared
NBO	Non-Bridging Oxygen
NIR	Near-Infrared
NPs	Nanoparticles
Nd_2O_3	Neodymium Oxide
Nd^{3+}	Neodymium Ions
OH	Hydroxide
PL	Photoluminescence
REIs	Rare Earth Ions
SAED	Selected Area Electron Diffraction
SPR	Surface Plasmon Resonance
TeO_2	Tellurite Dioxide
TiN	Titanium Nitride
Tm^{3+}	Thulium Ions
Nd^{3+}	Neodymium Ions
UV-Vis	Ultraviolet Visible
WO_3	Tungsten Oxide
XRD	X-ray Diffraction
ZnF_2	Zinc Fluoride
ZnO	Zinc Oxide

KESAN NANOPARTIKEL TITANIUM NITRIDA TERHADAP STRUKTUR & SIFAT OPTIK GELAS TELURIT YANG TERDOP BERSAMA NEODIMIUM/TULIUM

ABSTRAK

Keratan rentas pancaran yang kecil bagi kaca telurit terdop ion nadir bumi (REIs) menghalang penggunaannya dalam penguat gentian optik dan laser keadaan pepejal. Kajian membangunkan komposisi kaca baru dengan mengubah kepekatan nanozarah titanium nitrida (TiN NPs) pada 0.1 hingga 0.5 mol% dalam kaca tungsten-bismut telurit yang terdop bersama Nd^{3+} dan Tm^{3+}. Kaca ini telah disintesis menggunakan teknik perlindapan leburan, analisis struktur menunjukkan bahawa terdapat pengubahsuaian pada rangkaian kaca. XRD mengesahkan sifat amorfus kaca berdasarkan jalur lebar pada 20 – 40°, manakala puncak pada 36° menunjukkan kehadiran TiN NPs dalam kepekatan tinggi. HR-TEM menunjukkan saiz zarah dan taburan zarah, manakala spektra Raman dan FTIR mencadangkan penyahpolimeran rangkaian akibat kehadiran TiN NPs. Analisis optik (UV-Vis-NIR dan PL) menonjolkan peningkatan dalam sifat pancaran dan penyerapan. Peningkatan pancaran pada peralihan Tm^{3+}: $^3F_2 \rightarrow ^3H_6$ (648 nm) mencapai maksimum pada kepekatan 0.2 mol% TiN NPs iaitu sebanyak 3.13 kali ganda, didorong oleh kesan resonans plasmon permukaan setempat (LSPR). Analisis semi-empirik menggunakan teori Judd-Ofelt dan McCumber mengesahkan potensi bahan ini untuk aplikasi laser, menunjukkan keratan rentas pancaran dan pekali gandaan yang tinggi. Hasil kajian menekankan peranan penting pengubahsuaian struktur dalam meningkatkan prestasi optik, menjadikan kaca telurit yang dimodifikasi dengan TiN NPs sebagai calon berpotensi untuk laser keadaan pepejal, penguat gentian optik, dan teknologi inframerah dekat.

IMPACT OF TITANIUM NITRIDE NANOPARTICLES ON STRUCTURE & OPTICAL PROPERTIES OF NEODYMIUM/THULIUM IONS CO-DOPED TELLURITE GLASS

ABSTRACT

The small emission cross-section of rare earth ions (REIs)-doped tellurite glass limits its utilisation in optical fibre amplifiers and solid-state lasers. The study develops a novel glass composition by modifying concentrations of TiN NPs ranging from 0.1 to 0.5 mol% into tungsten-bismuth tellurite glasses co-doped with Nd^{3+} and Tm^{3+}. Glasses are synthesised via the melt-quenching technique. Structural analyses revealed modifications in the glass network. XRD confirmed the glass's amorphous nature with a broad hump at 20 – 40°, while a peak at 36° indicated the presence of TiN NPs at higher concentrations. HR-TEM revealed particle size and particle distribution, while Raman and FTIR spectra suggested network depolymerisation due to TiN NPs. Optical analyses (UV-Vis-NIR and PL) highlighted enhanced emission and absorption properties. Luminescence enhancement at Tm^{3+}: $^3F_2 \rightarrow {}^3H_6$ (648 nm) transition maximised at 0.2 mol% TiN NPs with 3.13-fold enhancement, driven by the localised surface plasmon resonance (LSPR) effect. Semi-empirical analyses using the Judd-Ofelt and McCumber theories validated the material's potential for laser applications, demonstrating high emission cross-sections and gain coefficients. The results underscore the critical role of structural modifications in enhancing optical performance, positioning TiN NPs-modified tellurite glasses as promising candidates for solid-state lasers, optical fibre amplifiers, and near-infrared technologies.

CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter presents the background of fibre optics and solid-state laser-based glass doped with rare-earth ions, and the motivation to carry out this work in the problem statement. This chapter also covers the research objectives, scope of the study, and significance of the study. The outline of the thesis is also provided.

1.2 Background Study

In recent years, visible to near-infrared solid-state lasers with fibre optics amplifiers have become advanced materials that require further improvement. Fibre optics has rapidly progressed due to its high usage in modern society, which facilitates data transmission, telecommunications, and internet connectivity. The information can be further transmitted over long distances with minimum loss of signal strength with the support of amplifier-based fibre optics. Fibre optics amplifiers are essential to telecommunication networks, high-speed internet connections, and efficient data transmission in healthcare, finance, and manufacturing industries (Blanc et al., 2023). High-speed data transmission capabilities and low latency make fibre optics amplifiers crucial for supporting the massive amount of data generated by these technologies. One of the fibre optics amplifiers is an erbium-doped fibre amplifier (EDFA), which is used in the wavelength division multiplexing (WDM) systems. It is the most commonly used type of fibre optics amplifier for long-distance communication systems, where its range lies in the C-band (1530 – 1565 nm) and broadens to the L-band (1565 – 1605 nm) (X. Liu, 2019). EDFA operates by using a length of optical fibre doped with erbium ions, which can be optically pumped to amplify the incoming signals. However, some modifications to optical fibre amplifiers (which are usually made by rare-earth-doped glass) need to be made to catch up with the expeditious emergence of communication technology by lowering the loss window and amplifying the signals of the optical carrier even more so that data transmission can travel at greater distances efficiently (Shen, Zhang, et al., 2020).

The development of 1.8 μm solid-state lasers has gained significant attention due to their potential applications, including laser ranging, air pollution monitoring, and eye safety surgery (Tang et al., 2022). Furthermore, laser gain media with broadband emission spectra have been employed in solid-state lasers to generate broadband lasers, enabling applications such as terahertz generation, optical communications, sensing, biomedical applications, optical coherence tomography (OCT) imaging, and other applications (L. Zhang et al., 2025). Solid-state laser advancements have also transformed the medical field, particularly through non-invasive techniques like thermography, photothermal therapy, and laser ablation. These methods are essential for monitoring skin temperature variations and critical in both thermoregulation studies and clinical diagnostics, such as cancer cell and solid tumour treatment (Peng et al., 2024; Pokharel et al., 2024; Thomas et al., 2023; J. Zhang et al., 2025). Thermography, for instance, provides real-time, two-dimensional imaging to identify abnormalities such as inflammation or altered blood flow. It is highly effective for lesion assessment, uncovering hidden issues, enabling an early diagnosis, and tracking postoperative treatment progress. By delivering quantitative data, thermography improves diagnostic accuracy and supports effective disease monitoring, emphasising its role in contemporary medical practices (Pokharel et al., 2024). The non-contact and radiation-free nature of these methods ensures the safety for both patients and healthcare providers, making them ideal for precise applications like surgical procedures (Peng et al., 2024). Light sources in the near-infrared (NIR) region are often used, typically within the first biological window (700–950 nm) and the second (1100–1400 nm). These ranges reduce photon interactions with water, haemoglobin, and melanin in the body, enabling greater light penetration into targeted tissues (Pokharel et al., 2024). However, high-energy solid-state lasers face challenges such as amplified spontaneous emission (ASE) due to their high pump power densities. ASE limits the energy storage capacity of the laser medium and reduces efficiency. The goal of addressing this issue involves developing laser media with optimised emission cross-sections (Tan et al., 2024).

Glass is essential in the fabrication of optical fibre amplifiers and solid-state lasers, which allow light signals to be transmitted over long distances with low loss signal quality. Glass, in general, is defined as a noncrystalline solid that, once in molten form, is then quenched rapidly without going through crystallisation (Masayuki & Yoshiyuki, 2000). It is often more favourable than crystals in the use in fibre optics and solid-state lasers due to its low cost, high flexibility, composition, size, shape, high transparency, can be incorporated with rare-earth ions, and high flexibility (Lakshminarayana et al., 2021; Yuliantini, Djamal, et al., 2018). Moreover, doping the glass with rare-earth ions boosts the emission cross-sections and gain coefficients, besides providing broad absorption and emission bands (Lakshminarayana et al., 2021). Therefore, determining the appropriate host glass material for designing rare-earth-doped glass is critical for enhancing the luminescent properties. The tellurite-based glass shows remarkable internal structural units that play a part in luminescence enhancer properties with a wide transmittance window in the infrared window, high compatibility with rare earth ions, higher refractive index, gain characteristics, high chemical stability and excellent infrared transmittance (Abuallan et al., 2023; Sharma et al., 2022; C. Zhang, Han, Wu, et al., 2022) To prevent signal attenuation at the infrared band, the phonon energy of host glass should be low so the stimulated emission cross-section increases. Tellurite glass is favourable due to its lowest phonon energy of about 750 cm^{-1}, contrary to other glasses such as silicate (about 1100 cm^{-1}), borate (about 1350 cm^{-1}), phosphate (about 1200 cm^{-1}), and germanate (about 900 cm^{-1}) (D. Zhao et al., 2023a). These qualities indicate that tellurite is a promising host glass for applications.

Rare-earth ions doped glass materials have been attracting attention owing to their versatile applications in photonics. To come up with optical fibre amplifier and solid-state laser applications, the rare-earth ions should be selected according to their energy transition, ability to increase the emission cross-section, and wavelength region. The neodymium ion (Nd^{3+}) emits energy at ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, which makes it among the right candidates to be doped for optical amplifiers and communications applications since it falls in the infrared (IR) wavelength range, specifically their emission bands at 900, 1060, and 1340 nm (Kamimura et al., 2017; Madhu, Al-Dossari, et al., 2023). Nd^{3+} ion can enhance optical properties because of its high quantum efficiency, high chemical, and thermal stability (Sailaja et al., 2022). These materials are useful for establishing stable glass that efficiently amplifies light. Another attractive rare-earth ion is thulium ions (Tm^{3+}). It radiates at 1800 and 2300 nm through the ${}^3F_4 \rightarrow {}^3H_6$ energy level transition, which is in the range of broadband amplifier applications (Basavapoornima et al., 2020). Other applications of Tm^{3+}-doped glass arise from its ${}^3F_4 \rightarrow {}^3H_6$ emission at 1.8 – 2.3 μm. This eye-safe band coincides with an atmospheric transmission window, making it suitable for LiDAR and range-finding systems (Iwai & Aoki, 2023; K. Li et al., 2023; Sohail et al., 2024). In remote sensing, these emissions overlap with absorption lines of CO_2 (~2.06 μm) and H_2O, enabling sensitive detection through DIAL and related methods (Fleurbaey et al., 2020; Howes et al., 2023). Military applications also exploit the 2 μm region for target designators and laser rangefinders, combining reduced ocular hazard with efficient long-range operation (Sohail et al., 2024). These two rare earth ions have been getting recognised recently, as there are some studies done due to their near infrared (NIR) transmission window. For instance, J. Ding et al., in 2022, examined whether under 808 nm laser excitation, these ions contributed to ultra-broadband luminescence bands observed in the near-infrared spectral range. Nd^{3+} and Tm^{3+} enhanced the luminescence bands from 1300-1600 nm and 1600-2200 nm, respectively. Their broad overlapping luminescence bands, covering the O, E, and S+C bands, can enhance the performance of optical fibre amplifiers by carrying more data (Ding et al., 2023).

Previous works have shown that the luminescence of rare-earth-doped glass can be enhanced by incorporating nanoparticles (NPs) into the glass (Mawlud et al., 2024; D. Zhao et al., 2023b). This is due to the localised surface plasmon resonance (LSPR) phenomenon, where the mechanism works when there is resonance between the incident electromagnetic radiation and the excited surface electrons on the NPs. Therefore, it leads to an enhancement of the local electromagnetic field or the local field effect (J. Liu et al., 2021). The most conventional plasmonic materials are gold (Au) and silver (Ag). They have been explosively popular due to their chemical stability and visible light resonance. The most conventional metallic NPs used in rare-earth-doped glass are gold (Au) and silver (Ag) due to their high conductivity, chemical stability, low dielectric losses, and lie in the visible wavelength region (Machado et al., 2019). However, these two popular NPs have drawbacks, such as poor thermal stability, high cost, easy oxidation, and visible window (Naldoni et al., 2017). These limitations make them less attractive for large-scale integration in photonic devices and glass-based hosts where high thermal stability and broad spectral tunability are required (Beierle et al., 2019).

In search of alternatives, transition metals such as titanium (Ti) have been considered due to their abundance, low cost, and potential to interact with the glass matrix. Ti NPs appear promising for optical enhancement; however, their intrinsic properties impose critical limitations. Their structural behaviour and solid-state properties significantly limit their effectiveness. Pure Ti possesses a hexagonal close-packed (HCP) crystal lattice and readily oxidises into TiO_2 during high-temperature glass melting. This oxidation often transforms Ti into network-forming Ti–O species, which reduce non-bridging oxygens (NBOs) critical for REIs luminescence and disrupt the structural and optical integrity of the glass (Ali et al., 2019; Chanakya et al., 2025; Gupta et al., 2017; Maltsev et al., 2025). Moreover, Ti lacks the robust electronic structure needed to sustain strong plasmonic behaviour, and its tendency to oxidise further compromises any plasmonic activity (Günaydın et al., 2024).

To address these challenges, titanium nitride (TiN) has emerged as a compelling alternative. Unlike pure Ti, TiN exhibits a rock-salt (NaCl-type) face-centred cubic (fcc) crystal structure that imparts high mechanical hardness, thermal stability, and resistance to oxidation. TiN's high melting point (~3220 K) and resistance to atomic diffusion and corrosion make it a formidable refractory material (Guo et al., 2019; Mohammadpour et al., 2018). Structurally, TiN remains stable even under harsh conditions, resisting oxidation up to approximately 800 °C, which is a clear advantage over Ti (Guo et al., 2019; Mohammadpour et al., 2018). From a solid-state perspective, TiN boasts a metallic electronic structure, with partially filled Ti 3d orbitals and strong p–d hybridisation with nitrogen, leading to high electrical conductivity and low resistivity (Guo et al., 2019). These qualities make TiN plasmonically active, supporting localised surface plasmon resonance (LSPR) and surface plasmon polariton (SPP) modes in the visible to near-infrared (NIR) spectrum, attributes desirable for enhancing rare-earth ion transitions in glass (Günaydın et al., 2024; Guo et al., 2019; Judek et al., 2021).

Recent research has therefore placed increasing emphasis on TiN NPs due to their multifunctional properties. TiN NPs have been applied in areas, notably photodetection, nonlinear optics, and biomedicine (Zakomirnyi et al., 2018). Compared to conventional noble metal nanoparticles, TiN NPs demonstrate superior thermal endurance, high electrical conductivity, chemical stability, mechanical robustness, and corrosion resistance, all while remaining cost-effective (Bayon et al., 2022). Most importantly, unlike Au and Ag, TiN NPs govern their LSPR peaks in the NIR region, which is important for photonic materials operating at the telecommunication range (Zakomirnyi et al., 2018). The advantages of TiN over Au and Ag NPs have motivated research into its impact on rare-earth-doped tellurite glass for fibre optics and solid-state lasers, which has not yet been studied.

In this research, we aimed to study the structural and spectroscopic properties of oxyfluorotellurite glass doped with neodymium and thulium ions by incorporating titanium nitride nanoparticles. The fabrication of tellurite glass is believed to magnify the emission cross-section for optical fibre amplifiers and solid-state lasers to support the transmission of data over long distances without signal loss. The pitfall of the current issues in the field of fibre optics, such as the high cost of nanoparticle embedding, can be addressed by studying alternative nanoparticles as LSPR sensitisers.

1.3 Problem Statements

The problem that this study addresses is the challenge posed by the inherent limitations of rare-earth ions doped tellurite glass for fibre optics and solid-state laser applications. $Tm^{3+/}Nd^{3+}$-doped tellurite glass, while possessing excellent luminescence properties ranging from Vis to NIR, it suffers from a relatively low absorption cross-section, which consequently results in a reduced emission gain and limited amplification efficiency (C. Li et al., 2023). Furthermore, the local glass network structure significantly affects the optical behaviour of the doped rare earth ions; a highly disordered or overly polymerised glass matrix can introduce non-radiative decay pathways, suppressing photoluminescence and reducing overall efficiency. Previously, metallic nanoparticles were integrated within REIs doped glass to use their localised surface plasmon resonance (LSPR) effect to enhance their PL intensity (J. Liu et al., 2021). Even though metal nanoparticles such as gold (Au) and silver (Ag) nanoparticles are frequently used in research, they possess drawbacks such as being expensive, easily oxidised and limited to the visible range (Naldoni et al., 2017). Recently, titanium nitride nanoparticles (TiN NPs) appeared as a potential candidate as an alternative to the aforementioned metallic nanoparticles; however, their potential as a new alternative LSPR sensitiser is less explored. Titanium nitride nanoparticles (TiN NPs) are estimated to enhance the emission cross-section of the rare earth ions doped tellurite glass due to their LSPR estimated at around 730 nm, which is near to Nd^{3+} excitation wavelength that could support Tm^{3+} ion luminescence, yet has not been fully studied (Jiang et al., 2019). In addition to this luminescence enhancement, TiN NPs may also modify the structural network of the host glass, potentially influencing the local symmetry and ligand field environment around REIs, thereby altering optical transitions. The research explores the potential of TiN NPs in modifying the optical and structural properties of Tm^{3+}/Nd^{3+}-doped oxyfluorotellurite glass, which is prospective as a new optical gain for telecommunications.

1.4 Research Objectives

This work investigates the structural and optical modifications of Tm^{3+}/Nd^{3+}-doped tungsten-bismuth tellurite glasses embedded with TiN NPs at concentrations ranging from 0.0 to 0.5 mol%. The specific objectives of this research are as follows:

i. To verify the presence of TiN NPs and the modifications in vibrational bonding of Nd^{3+}/Tm^{3+}-doped oxyfluorotellurite glass using X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy.

ii. To evaluate the influence of TiN NPs on the physical and optical behavior of the glass system by examining parameters such as density (via Archimedes' method), refractive index (via Dimitriv-Sakka relation), optical band gap and Urbach energy (via UV-Vis-NIR spectroscopy), along with photoluminescence intensity and emission characteristics (via PL spectroscopy).

iii. To evaluate the radiative transition probabilities, emission cross-sections, bandwidth gain, and the spectroscopic quality factor of the glasses using Judd–Ofelt theory.

iv. To evaluate the absorption cross-section, stimulated emission cross-section, and gain efficiency of the glasses using McCumber theory.

1.5 Scope of Study

The scope of this study focuses on preparing samples by using the melt-quenching technique to prepare tellurite glass doped with Nd^{3+} and Tm^{3+} REIs, and embedded with TiN NPs. Density is measured by Archimedes' principle, while the refractive index is determined using the Dimitrov-Sakka equation. This study is also divided into two sections: structural and optical properties. The nature of the glass is clarified using XRD. The existence of TiN NPs in the rare earth ions-doped tellurite glass was probed through HR-TEM, while the assigned vibration bonding was done using a FTIR spectrophotometer and Raman spectroscopy. For the optical properties, the absorption and emission spectra were obtained by using UV-Vis-NIR and PL spectroscopy, respectively. Some parameters, such as emission cross-section, emission gain, spectroscopic quality, radiative probabilities, and quantum efficiency of the prepared samples using Judd-Ofelt theory to evaluate the suitability of the glass as a solid-state laser and fibre optic material. Other parameters, notably the absorption and emission cross-sections, gain coefficient, gain bandwidth, and gain figure of merit of the prepared glass, will further be analysed using McCumber theory to validate its performance as a gain medium. In summary, this research aims to contribute to fibre optic technology and other solid-state applications.

1.6 Significance of the Study

The significance of the presence study led to the search for alternative materials as sensitisers with a tunable LSPR range. Incorporating TiN NPs into rare-earth-doped tellurite glass offers insights into its potential as an alternative to common gold and silver nanoparticles for major-scale glass manufacturing. In addition, this study investigates the influence of LSPR in the context of fabricating the optical properties of Nd^{3+}/Tm^{3+}-doped oxyfluorotellurite glass. The enhancement of the structural and optical properties of glass may also contribute to the knowledge of photonics materials, especially in the field of fibre optics and various solid-state applications.

1.7 Thesis Outline

The thesis comprises five chapters and is outlined as follows:

Chapter 1 is an introductory chapter that summarises the research context by highlighting fibre optics and solid-state laser applications, glass, rare-earth ions, and nanoparticles. This chapter discusses the problem statements, research objectives, scope of the study, and significance of the study.

Chapter 2 reviews the literature on the past studies of tellurite glass, modifiers, rare-earth ions, metal nanoparticles, titanium nitride micro-nanoparticles, Judd-Ofelt theory, and McCumber theory.

Chapter 3 describes the experimental methods and is divided into three main parts. The first section discusses the preparation of glass samples by the melt-quenching technique. The second section investigates the physical, structural, and optical properties of the glass samples using various instruments. This includes the verification of the existence of TiN NPs and their luminescence aspects. The third section is a semi-empirical analysis by employing Judd-Ofelt and McCumber theories. This part is useful for data analysis.

Chapter 4 presents the analysis and discussion of the experimental results, focusing on the physical and structural properties of Tm^{3+}/Nd^{3+}-doped tungsten-bismuth tellurite glasses with ZnF_2 and TiN NPs. Structural characterisation through Raman, FTIR, XRD, and TEM revealed network depolymerisation, NBO formation, and localised crystallinity. The optical properties were examined via UV-Vis-NIR and PL spectroscopy, focusing on rare-earth ion transitions and luminescence enhancements. Semi-empirical analyses using Judd-Ofelt theory and McCumber analysis quantify radiative transitions and quantum efficiency, demonstrating the potential of these glasses for solid-state laser, photonic, and radiation shielding applications.

Chapter 5 presents the conclusions of this study and outlines recommendations for future research. This section begins by summarising the key findings related to the structural, optical, and photoluminescence properties of the synthesised materials, highlighting their importance in the context of advanced material design for photonic and optoelectronic applications. The broader implications of the findings are discussed, with a particular focus on their contributions to understanding the behaviour of rare-earth ions in modified glass matrices. The limitations encountered during the study are also addressed, providing insights into potential areas for improvement. Finally, recommendations are proposed to guide future work, including optimising material synthesis processes, investigating alternative dopants or structural modifiers, and conducting long-term stability assessments to enhance the practical applications of these glass systems.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter discusses a brief literature review regarding tellurite glass, modifiers such as tungsten oxide, WO_3, bismuth oxide, Bi_2O_3, zinc oxide, ZnO, and zinc fluoride, ZnF_2, rare earth ions such as neodymium and thulium ions, transition metal nanoparticles, titanium nitride micro-nanoparticles, and theories used for semi-empirical analysis, notably Judd-Ofelt theory and McCumber theory.

2.2 Tellurite Glass

The rising optical interest of tellurite glass in solid-state lasers and fibre optics is ever-increasing (Azlina et al., 2020). Tellurite glass is particularly well-suited for speciality optical fibres, supercontinuum generation, and laser devices, as well as for the nonlinear conversion of mid-IR ultrashort optical pulses (Wang et al., 2016; Anashkina et al., 2020). The advancement of multi-material fibres that integrate optical waveguide properties and in-fibre electrical excitation has the potential to offer a range of cutting-edge signal processing, sensing or imaging functionalities by utilising tellurite glass (Maldonado et al., 2020). Tellurite-based glass possesses several advantageous characteristics. Some advantages of this material are a lower melting temperature, lower phonon energy, improved chemical stability, a larger refractive index, a wide gearbox window (350-6500 nm), high thermal stability, and an exceptional internal structural unit that enhances the solubility of rare earth ions. Consequently, the occurrence of the concentration quenching phenomenon declines (Jakutis et al., 2010; Mao et al., 2020; Stepien et al., 2011).

Tellurite glasses are noncrystalline solids that offer various applications owing to their excellent optical and physical properties (Wang, P., Jia, S., Lu, X., Jiang, Y., Yu, J., Wang, X., Wang, S., Lewis, 2020). Contrary to recent research in 1952, tellurite glasses were seen as intermediate glass forms and attracted no attention, as tellurite dioxide, TeO_2, the main raw material at that time, was expensive to produce (Lambson et al., 1984; Stanworth, 1952). However, the glasses made some progress in the 1990s due to the advancements and understanding of the optical and physical properties of the new tellurite glasses (Mori et al., 1997; J. S. Wang et al., 1994). This involves developing new materials by modifying TeO_3 glass with rare-earth oxides (REO) or transition metal ions (TMI) to obtain unique optical, electrical, thermal, elastic, and vibrational properties, as well as applications. They have paved the way for semiconducting tellurite glass research (El-Mallawany, 2018). Tellurite glasses are receiving international attention for their potential applications in areas of optoelectronics, namely, laser technology and fibre optics (Rivera, V. A. G., Maanzani, 2017).

TeO_2 is classified as a conditional glass former because it cannot independently form a glassy structure. However, its glass-forming ability and stability are improved by the introduction of modifiers such as alkali oxide, alkaline earth oxide, halide, and sulfate (Bassam et al., 2023; Hosny et al., 2024). This limitation arises from the presence of a lone-pair electron (LPE) on Te^{4+}, which restricts the number of structural configurations capable of forming a glassy network. The multivalent nature of Te^{4+}, influenced by the LPE, contributes to the rigidity of the vitreous structure while also minimising the electrostatic repulsion caused by the lone-pair electron (Chacaliaza-Ricaldi et al., 2023). TeO_2 consists of three fundamental structural units, each associated with an LPE: i) TeO_4 (Trigonal Bipyramid, tbp): this unit comprises four oxygen atoms covalently bonded to a central Te atom, forming a trigonal bipyramidal structure; ii) TeO_3 (Trigonal Pyramid, tp): created when certain Te–O bonds break, forming trigonal pyramids. These consist of two bridging oxygens (BO) and one non-bridging oxygen (NBO), the latter being a Te=O double bond; iii) $TeO_{3+\delta}$ (Intermediate Polyhedra): this structure arises due to distortion of the trigonal bipyramid caused by excess oxygen, δ (Chacaliaza-Ricaldi et al., 2023). In other words, the incorporation of additional oxides into base glass compositions can be categorised into three distinct roles: network modifiers, intermediates, and network formers. This classification is primarily determined by the single bond strength of the oxide, where a higher bond strength significantly enhances the glass-forming tendency (Effendy et al., 2021). Besides, the ability of [TeO_4] units to transform into [TeO_3] trigonal pyramids under specific conditions adds adaptability to the glass network, enabling the development of materials with finely tuned physical and optical properties. The structural units in the alkali tellurite crystals are depicted in Figure 2.1.

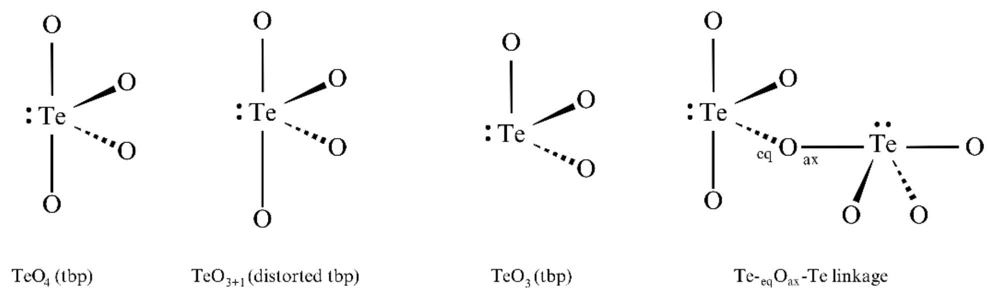

Figure 2.1 Alkali tellurite crystal structural units.

Unlike conventional glass systems such as silicates, borates, and phosphates, tellurite glasses exhibit a unique combination of high refractive index, low phonon energy, broad infrared transmission range, and excellent chemical and thermal stability.

The low melting point, higher refractive index, low photon energy, high dielectric constant, good mechanical strength, good chemical durability, good transmission in both visible and infrared wavelength regions, superior thermo-optic coefficient, and great third-order non-linear optical properties were some of the physical, structural, and optical properties of this based glass former (Effendy et al., 2021). The table below shows the comparison of various host glasses with certain parameters (Alharshan et al., 2024; Attallah et al., 2024; Egan, 2024; He et al., 2019; Hraiech et al., 2018; Huerta et al., 2024; Jiménez et al., 2024; Kaniyarakkal et al., 2023; Kut'in et al., 2019; Lakshminarayana et al., 2020; Monisha et al., 2020; Rajaramakrishna et al., 2019; Shen, Cheng, et al., 2020; C. Song et al., 2023; Sun et al., 2024; Ye et al., 2023; Yuliantini, Djamal, et al., 2018; C. Zhang et al., 2024)

Table 2.1 Comparison of tellurite host glass with other host glasses.

Host Glass	**Refractive index**	**Trans-mission Window**	**Phonon Energy**	**Rare-Earth Solubility**	**Thermal Stability**	**Chemical Stability**	**References**
Silicate	Low (1.65)	Moderate (2000 – 3000 nm)	High (1100 cm^{-1})	Moderate (1.6×10^{20} ions/cm^3)	Low (0.59×10^{-6} K^{-1})	High	(Egan, 2024; Rajaramakrishna et al., 2019; Shen, Cheng, et al., 2020; C. Song et al., 2023; Sun et al., 2024)
Tellurite	High (2.09)	Wide (9350 – 6500 nm)	Low (780 cm^{-1})	High (4.0×10^{20} ions/cm^3)	High (54.60 10^{-6} K^{-1})	High	(He et al., 2019; Kaniyarakkal et al., 2023; Kut'in et al., 2019; Ye et al., 2023; Yuliantini, Djamal, et al., 2018)
Borate	Low (1.54)	Moderate (1050 – 1400 nm)	High (1380 cm^{-1})	Moderate (1.4×10^{20} ions/cm^3)	High (42.00×10^{-6} K^{-1})	High	(Alharshan et al., 2024; Attallah et al., 2024; Lakshminarayana et al., 2020; Monisha et al., 2020; Yuliantini, Djamal, et al., 2018)
Phosphate	Low (1.46)	Moderate (~200 – 2500 nm)	High (~1200 cm^{-1})	Moderate (1.3×10^{20} ions/cm^3)	High (14.00×10^{-6} K^{-1} to 15.00×10^{-6} K^{-1})	Low	(Hraiech et al., 2018; Huerta et al., 2024; Jiménez et al., 2024; C. Zhang et al., 2024)

Prior research has indicated that the inclusion of a modifier like BaF_2 with fluoride contents has the potential to lower the phonon energy of the host glass, elevate the doped rare-earth ions in the glass matrix contents, and alleviate the adverse effects of hydroxide on luminescence (Fu et al., 2019; C. Zhang, Han, Wu, et al., 2022). According to G. Wang et al., reported that the inclusion of ZnF_2 and rare earth oxides in oxyfluorotellurite glasses can greatly enhance their thermal and optical properties

(Klimesz et al., 2018; G. Wang et al., 2005). The introduction of fluorine to the TeO_2-based oxide glass system decreases the connectivity of the tellurite former network. The transformation of the trigonal bipyramid TeO_4 through TeO_{3+1} to the trigonal pyramid TeO_3 leads to a reduction of Te-O-Te linkages. In addition, the glass structure of the host and the coordination of the REIs are altered by the presence of F^- and O^{2-} anions (Klimesz et al., 2018). Therefore, tellurite, based on oxygen and fluorine, is an appealing candidate for further studies using the selected modifiers.

2.3 Modifiers

2.3.1 Tungsten Oxide (WO_3)

Metal oxides such as WO_3 can prevent crystallisation, which has been appealing for glass composition. It enhances the density and refractive index, improves the glass transition temperature, mechanical properties, and reduces the non-radiative losses (Biswas & Jana, 2023; C. Li, Zhang, et al., 2022). The structural units formed as WO_3 modified in the glass matrices are WO_4 and WO_6 (Kotb et al., 2023). In the presence of WO_3, the quantum efficiency of the tellurite glasses can be enhanced by reducing the non-radiative losses (Ghosh et al., 2022). In the work reported by Ren et al. in 2023, they showed that the introduction of WO_3 into bismuth-tellurite glass, the near-infrared emission can be effectively enhanced (Ren et al., 2023). Previous works on tungsten tellurite glass are reported in (Biswas & Jana, 2023; Chacaliaza-Ricaldi et al., 2023; L. Xu et al., 2023).

2.3.2 Bismuth Oxide (Bi_2O_3)

Bi_2O_3, a heavy metal oxide similar to WO_3, is a versatile modifier that has garnered significant attention in various fields due to its unique properties (Komatsu et al., 2020). The addition of the Bi_2O_3 into the host glass matrix will increase density, moisture resistance, refractive index, and prevent crystallisation (Ali et al., 2023; Sayyed, D'Souza, et al., 2022). According to Brand *et al.*, they imply the higher polarisability of Bi^{3+} ions causes the increment in linear and nonlinear refractive indices (Brand et al., 2023). Besides, there are two potential coordinations, such as pyramidal [BiO_3] and octahedral [BiO_6] units, which indicate how these units can work as both glass formers and modifiers in glass, as Bi_2O_3 is classified as the conditional glass-forming oxide (Ali et al., 2023; Komatsu et al., 2020). Bismuth-tellurite glass can be considered the most convenient material for near-infrared emission due to its properties, such as low phonon energy, highly concentrated rare-earth doping (Ren et al., 2023). The applications of Bi_2O_3 incorporation include superconductivity, radiation shielding, piezoelectricity, solid-state lasers, and fibre optics communication (Ali et al., 2023).

2.3.3 Zinc Oxide (ZnO)

ZnO has attractive properties, notably, non-toxicity, high transparency in the visible region, high chemical and thermal stability, high refractive index, and absorption edge (Amakali et al., 2020). As a modifier oxide, ZnO can disrupt the Te-O bond and create non-bridging oxygen atoms by converting TeO_4 trigonal bipyramidal units into TeO_3 trigonal pyramids. The restructure of the tellurite network enhances the density and reduces optical band gaps related to the coordination states of the structure, including ligand field strengths, local site symmetry, and variations in the nearest-neighbour environment (Brand et al., 2023; Clabel H et al., 2021; Effendy et al., 2021). Studies related to zinc tellurite glasses have been reported (Mhareb et al., 2023; Nazrin et al., 2024; Shoaib, Khan, Iskakova, et al., 2022).

2.3.4 Zinc Fluoride (ZnF_2)

The melt-quenching technique in the glass preparation raises a concern about the presence of the OH^- groups in the glass, which may affect the spectroscopic efficiency and transparency in the infrared region (Pinto et al., 2024). As depolymerisation of the glass structure may occur and create non-bridging oxygens (NBOs) at higher concentrations of fluorine, either when double-valence oxygen is occupied with single-valence fluorine or during modifier ion filled in the interstitial sites, the addition of zinc will avoid it completely (Neethish et al., 2021). Nevertheless, the replacement of ZnO with ZnF_2 could be attractive, where the combination of oxide and fluoride anion reduces the phonon energy while maintaining the chemical stability of the glass. It was reported that among fluorides, ZnF_2 is an effective reagent to withdraw hydroxyl groups and suit laser host materials (Huang et al., 2018). Therefore, oxyfluoride glass is highly appealing due to its unique thermo-optical properties and ability to dissolve high concentrations of rare earth metals, resulting in transparency across a wide range of wavelengths (Kolobkova et al., 2021).

2.4 Rare Earth Ions

The exceptional luminescence characteristics exhibited by rare earth ion (REI)-based luminescent materials have garnered considerable interest in the field of optical gain. Selecting the right host material is crucial for REIs embedded glass systems to exhibit exceptional luminescence and effectively utilise their applications in light-matter interaction, such as fibre lasers and laser amplifiers (Kaniyarakkal et al., 2023). Thulium (Tm^{3+})-doped REI glasses exhibit exceptional luminescence properties, making them highly versatile for various applications. The 1.2 μm emission from the $^1G_4 \rightarrow {}^3H_4$ transition enhances optical fibre amplifiers by increasing data transmission rates and extending coverage, thereby boosting system capacity (Jamalaiah, 2025; Ohishi et al., 1998). Additionally, Tm^{3+} exhibits broad fluorescence emission from the $^3F_4 \rightarrow {}^3H_6$ transition, covering 1500–2000 nm. This wavelength range is crucial for optical amplifier applications in the C-, L-, and U-bands (1535 – 1675 nm), widely used in telecommunication networks (Pinto et al., 2024; C. Zhang, Han, Wu, et al., 2022). The transmission loss in fibre optic communication for these wavelengths is illustrated in Figure 2.2 (Nouchi et al., 2003). Furthermore, high quantum efficiency in solid-state host matrices is critical for optimising the performance of 1.46 µm emissions, especially for S- and C-band telecommunications and visible laser source development (Jamalaiah, 2025). In addition to telecommunications, Tm^{3+} ions display fluorescence across red, blue, ultraviolet, and near-infrared (NIR) regions. These properties under visible or NIR excitation make them suitable for diverse applications, including colour displays, remote sensing, undersea optical transmission, visible lasers, biomedicine, military uses, optical data storage, light detection and ranging (LIDAR), and eye-safe laser radar systems (Gouveia-Neto et al., 2015; J. Li et al., 2007, 2009; Mariselvam & Liu, 2022). In particular, Tm^{3+}-doped fluorotellurite glass demonstrates strong potential for 1.8 µm solid-state lasers due to its high optical transmittance, low phonon energy, and extended fluorescence lifetime of Tm^{3+} ions (Tang et al., 2022). Tm^{3+}-doped tellurite glasses also show promise for blue light laser applications, owing to their visible and NIR fluorescence characteristics (Lakshminarayana et al., 2019, 2021; Mariselvam & Liu, 2022). Finally, the 2 µm Tm^{3+}-doped lasers have proven highly effective in healthcare, particularly for surgical procedures, due to their strong tissue interaction in the 1.92–1.94 µm wavelength range (Godard, 2007).

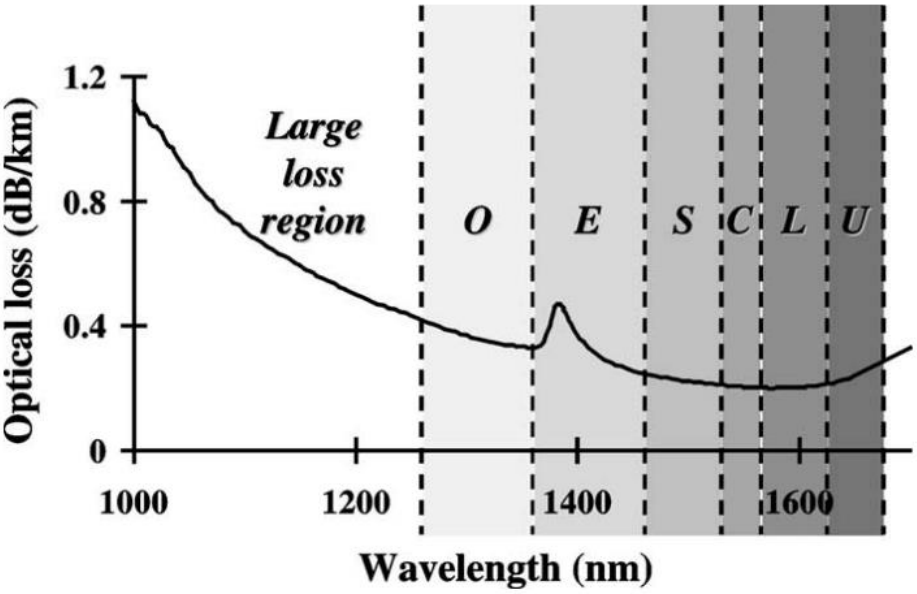

Figure 2.2 Transmission loss in optical fibre in fibre optic communication wavelength bands according to ITU-T definition (where *O* = Original, *E* = Extended, *S* = Short, *C* = Conventional, *L* = Long, and *U* = Ultra-long bands). Figure extracted from (Nouchi et al., 2003).

Neodymium ions (Nd^{3+}), other than their well-defined luminescence in NIR, can further boost photonic material performance because of their chemical stability within glass (Abuallan et al., 2023). In 1961, Snitzer laid the groundwork for understanding the laser properties of Nd^{3+} ion-doped glasses through his seminal research (Snitzer, 1961). Since then, oxide glasses doped with Nd^{3+} have attracted research interest, particularly because of their intense fluorescence bands at 800, 1060, and 1300 nm. These properties make them suitable for ultra-high-power and ultra-fast optical laser applications. (Prasad et al., 2020; Sailaja et al., 2022). Transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at 1060 nm is highly efficient and operates at a low threshold, making it an excellent choice for solid-state laser systems (Vijayatha et al., 2021). This emission is also strongly enhanced by Nd^{3+}-doped glass for lasing actions such as laser ablation in cosmetic medicine and therapy (Ismail et al., 2024). In fibre optics applications, the same transition also demonstrates one of the highest stimulated emission cross-sections, further enhancing its suitability for advanced telecommunications applications. Nd^{3+} ions contribute significantly to laser performance by reducing non-radiative decay via multi-phonon relaxation and energy transfer processes (Prasad et al., 2020; Yue et al., 2019). Research has indicated that Nd^{3+}-doped oxyfluorotellurite glass holds immense potential as a near-infrared laser gain medium, for optical telecommunication, and for imaging (Yuliantini, Djamal, et al., 2018). The exceptional radiation efficiency of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition underpins its wide-ranging utility in infrared optical communication systems, including waveguide lasers, optical data storage systems, fibre optics, and optical amplifiers (Madhu, Al-Dossari, et al., 2023).

The rationale for selecting Nd^{3+} and Tm^{3+} as the dopants in the studied glasses, in comparison to other REIs in the tellurite glasses, is detailed in Table 2.2 (Cao et al., 2023; Ren et al., 2023; C. Song et al., 2022; C. Zhang, Han, et al., 2023; C. Zhang, Zhang, et al., 2023; D. Zhao et al., 2023b; Zhou et al., 2022). The compositions designed by Zhao et al. outperformed emission cross-section among other compositions with a value of 1.24 $\times 10^{-20}$ cm^2, thereby improving the gain efficiency in fibre optics amplifiers more effectively (D. Zhao et al., 2023b).

Table 2.2 Comparison table of tellurite host glass with various REIs inclusion compositions.

Compositions (mol %)	**Emission Cross-Section ($\times 10^{-20}$ cm^2)**	**References**
$55TeO_2$–$15B_2O_3$–$10Al_2O_3$–$10Na_2O$–$0.5Tm_2O_3$	0.91(Tm^{3+})	(Cao et al., 2023)
TeO_2–15ZnO–$10Ga_2O_3$–$5La_2O_3$–$1Er_2O_3$-$3Yb_2O_3$	0.29 (Er^{3+})	(C. Zhang, Zhang, et al., 2023)
$75TeO_2$–$10Ga_2O_3$–$15BaF_2$–$0.75Tm_2O_3$	0.87(Tm^{3+})	(C. Zhang, Han, et al., 2023)
$61TeO_2$–28ZnO–$6.7WO_3$–$3.3Bi_2O_3$–	1.24 (Nd^{3+})	(D. Zhao et al., 2023b)

0.015Nd_2O_3–0.5Tm_2O_3–0.5AgCl		
49TeO_2–15Bi_2O_3–24B_2O_3–10BaF_2–2Yb_2O_3–0.75Tm_2O_3	0.98 (Tm^{3+})	(C. Song et al., 2022)
75TeO_2–5Bi_2O_3–10WO_3–10ZnO–2Yb_2O_3–0.5Ho_2O_3	1.15 (Ho^{3+})	(Ren et al., 2023)
81TeO_2–10Bi_2O_3–8Li_2O–1Er_2O_3	1.04(Er^{3+})	(Zhou et al., 2022)

2.5 Metal Nanoparticles

Nanoparticles (NPs), defined as particles with dimensions between 1 and 100 nm, have revolutionised the material science field because of their unique chemical, optical, electrical, and magnetic properties (Patil et al., 2022). This makes them different from bulk materials. One of the earliest applications of plasmons in metal NPs dates back to the 4th century, when the invention of the Lycurgus cup was created by the Romans. That spectacular glass was due to the presence of gold and silver NPs in the glass, causing different colours to radiate when the light reflected and transmitted (Verma et al., 2022). Besides, their inclusion in optical systems enhances light manipulation, amplification, and energy transfer, enabling breakthroughs in the wide field of micro-nano optical devices and functional substances, such as sensors, optoelectronics, biomedicine, catalysis, and so forth (Z. Wang et al., 2022).