

THE OPTICAL PROPERTIES OF ERBIUM DOPED ZIRCONIUM
OXYFLUORIDE TELLURITE GLASS EMBEDDED WITH SILVER
NANOPARTICLES

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This thesis is specially dedicated to:

My beloved parent,

Md Zain Banain, Surati A. Ghani

My supportive sister,

Nur Aina Balqis

My dedicated lecturer,

Prof. Dr. Md Rahim Sahar

and all my friend.

...thanks...

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ABSTRACT

Achieving enhanced optical properties of rare earth doped glass by the introduction of metal nanoparticle remains a challenging task. In addition, upconversion emission and infrared emission of erbium doped glass are ever-demanding for a large variety of optical applications. Therefore, in this study four series of erbium doped zirconium oxyfluoride tellurite glasses embedded with silver nanoparticles (Ag NPs) with composition of $(90-x)\text{TeO}_2 - 10\text{MgO} - (x)\text{ZrF}_4$ ($0 \leq x \leq 6$ mol%), $(84-y)\text{TeO}_2 - 10\text{MgO} - 6\text{ZrF}_4 - (y)\text{Er}_2\text{O}_3$ ($0 \leq y \leq 2$ mol%), $(88.5-z)\text{TeO}_2 - 10\text{MgO} - (z)\text{ZrF}_4 - 1.5\text{Er}_2\text{O}_3$ ($0 \leq z \leq 4$ mol%) and $(82.5-w)\text{TeO}_2 - 10\text{MgO} - 6\text{ZrF}_4 - 1.5\text{Er}_2\text{O}_3 - (w)\text{AgCl}$ ($0 \leq w \leq 1.0$ mol%) were prepared using melt quenching technique and investigated through optical characteristics. It is found that, the presence of a broad hump in X-ray diffraction (XRD) pattern confirms the amorphous nature of glass. HTEM images verify the existence of silver nanoparticles with two interplanar spacings about 0.20 nm and 0.23 nm corresponding to d_{111} and d_{200} spacing, respectively. The glass density and molar volume are found to be in the range of 4.11-5.09 g/cm³ and 29.1 to 36.9 cm³ mol⁻¹, respectively. It is also found that as the amount of zirconium fluoride is increased, the glass stability increases. The UV-Vis-NIR spectra reveal seven absorption bands centered at 486, 524, 544, 655, 803, 980 and 1526 which are assigned to the transition from ground state $^4\text{I}_{15/2}$ to the various excited levels $^4\text{F}_{7/2}$, $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$, $^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$, and $^4\text{I}_{13/2}$ respectively. Two surface plasmon resonances (SPR) are observed at 530 nm and 570 nm. The optical band gap energy, Urbach energy and refractive index have also been determined, and they were in the range of 2.23 – 3.05 eV, 0.09 – 0.50 eV and 2.384 - 2.650, respectively. The Judd-Ofelt intensity parameter, spontaneous emission probabilities, radiative lifetime and branching ratios of all transitions were calculated based on Judd-Ofelt theory. The upconversion ($\lambda_e = 980$ nm) emission and infrared ($\lambda_e = 633$ nm) emission peaks of Er^{3+} ion exhibit at 525 nm (strong green), 555 nm (moderate green), 657 nm (strong red) and 1530 nm (near-infrared), respectively. The zirconium oxyfluoride tellurite glass sample contains 1.5 mol% Er_2O_3 and 1.0 mol% of AgCl shows the highest enhancement in the emission peak of 1530nm ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$). The enhancement is attributed to the energy transfer from Ag nanoparticle to Er^{3+} ions. The result of the present work revealed that the investigated glass can be a potential material for photonic devices and solid state lasers.

ABSTRAK

Penghasilan sifat optik yang lebih baik bagi kaca berdopkan nadir bumi dengan menambah zarah nano logam merupakan tugas yang sentiasa mencabar. Di samping itu, pancaran penukaran ke atas dan pancaran inframerah bagi kaca berdopkan erbium sentiasa diperlukan bagi pelbagai jenis aplikasi optik. Oleh itu, dalam kajian ini empat siri kaca tellurite zirkonium oksifluorida berdopkan erbium oksida yang tertanam zarah nano perak (Ag NPs) dengan komposisi (90-x) TeO₂ - 10MgO - (x)ZrF₄ (0 ≤ x ≤ 6 mol%), (84-y) TeO₂ - 10MgO - 6ZrF₄ - (y)Er₂O₃ (0 ≤ y ≤ 2 mol%), (88.5-z) TeO₂ - 10MgO - (z)ZrF₄ - 1.5Er₂O₃ (0 ≤ z ≤ 4 mol%) dan (82.5-w) TeO₂ - 10MgO - 6ZrF₄ - 1.5Er₂O₃ - (w)AgCl (0 ≤ w ≤ 1.0 mol%) telah disediakan menggunakan teknik pelindapan leburan dan dikaji menerusi ciri optik. Kewujudan puncak yang lebar pada corak pembelauan sinar-X (XRD) membuktikan sifat amorfus kaca. Imej HTEM pula membuktikan kewujudan zarah nano perak dengan jarak dua satah 0.20 nm dan 0.23 nm yang masing-masingnya mewakili jarak d₁₁₁ dan d₂₀₀. Ketumpatan kaca dan isipadu molar didapati masing-masing berada di dalam julat 4.11 - 5.09 g / cm³ dan 29.1 - 36.9 cm³ mol⁻¹. Turut ditemui bahawa apabila jumlah zirkonium fluorida meningkat, kestabilan kaca turut meningkat. Spektrum UV-Vis-NIR menunjukkan tujuh jalur serapan yang berpusat di 486, 524, 544, 655, 803, 980 dan 1526 nm yang mewakili transisi daripada keadaan asas ⁴I_{15/2} kepada pelbagai keadaan teruja ⁴F_{7/2}, ²H_{11/2}, ⁴S_{3/2}, ⁴F_{9/2}, ⁴I_{9/2}, ⁴I_{11/2} dan ⁴I₁₃. Dua puncak resonans plasmon permukaan (SPR) diperlihatkan pada 530 nm dan 570 nm. Jurang tenaga optik, tenaga Urbach dan indeks biasan juga telah ditentukan, dan masing-masing berada dalam lingkungan 2.23 – 3.05 eV, 0.09 – 0.50 eV dan 2.384 - 2.650. Pembolehubah keamatan Judd-Ofelt, kebarangkalian pancaran spontan, jangka hayat radiatif dan nisbah cabang bagi semua transisi telah dikira berdasarkan teori Judd-Ofelt. Pancaran penukaran ke atas (λ_e = 980 nm) dan pancaran inframerah (λ_e = 633 nm) mempamerkan puncak bagi ion Er³⁺ masing-masing pada 525 nm (hijau kuat), 555 nm (hijau sederhana), 657 nm (merah kuat) dan 1530 nm (inframerah). Sampel kaca tellurite zirkonium oksifluorida yang mengandungi 1.5 mol% Er₂O₃ dan 1.0 mol% AgCl menunjukkan peningkatan pada puncak pancaran yang jelas pada 1530 nm (⁴I_{13/2} → ⁴I_{15/2}). Penambahan ini disebabkan oleh pemindahan tenaga daripada zarah nano Ag kepada ion Er³⁺. Hasil daripada kerja ini, membuktikan bahawa kaca yang diselidiki merupakan bahan berpotensi untuk peranti fotonik dan laser keadaan pepejal.

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LIST OF SYMBOLS

λ	-	Wavelength
θ	-	Diffraction angle
ρ_l	-	Liquid density
ρ	-	Sample density
W_a	-	Weight of sample glass
W_l	-	Weight of sample in liquid
V_m	-	Molar volume
M	-	Molar weight
α	-	Absorption coefficient
d, L	-	Thickness of sample
A	-	Intensity absorption
$\hbar\omega$	-	Photon energy
ω	-	Frequency dependent
m	-	Index value ($m = 1/2, 3/2, 2$ or 3)
B	-	Constant
n	-	Refractive index

D	-	Crystalline size
T_g	-	Glass transition temperature
T_x	-	Onset crystalline transition temperature
T_c	-	Crystalline transition temperature
T_m	-	Melting temperature
ΔT	-	Thermal stability
ΔE	-	Urbach energy
E_{opt}	-	Optical band gap energy
E'_{opt}	-	Optical band gap energy between tail
h	-	Planck's constant
c	-	Velocity of light in vacuum
m	-	Rest mass of electron
ν	-	Mean energy of transition in cm^{-1}
J	-	Total angular momentum quantum number
S	-	Spin angular momentum quantum number
L	-	Orbital angular momentum quantum number
f_{cal}	-	Calculated oscillator strength
f_{exp}	-	Experimental oscillator strength
Ω_λ	-	Judd Ofelt parameter
e	-	Electron charge
I	-	Intensity

I_o	-	Intensity of first sample
I_i	-	Integrated intensity
K	-	Wave number
τ_r	-	Radiative lifetime
S_{ed}	-	Electric dipole line strength
A_{ed}	-	Electric dipole transition
A_{md}	-	Magnetic dipole transition
β	-	Branching ratio
Q	-	Quality factor
σ_{em}	-	Stimulated emission cross section
λ_{peak}	-	peak emission
$\Delta\lambda_{eff}$	-	Effective bandwidth
A_{tot}	-	total spontaneous transition probability
C_2^i	-	Reduced matrix element

LIST OF ABBREVIATIONS

NBO	-	Non Bridging Oxygen
BO	-	Bridging Oxygen
XRD	-	X -ray Diffraction
UV	-	Ultra Violet
Vis	-	Visible
IR	-	Infrared
NIR	-	Near Infrared
TEM	-	Transmission Electron Microscopy
HRTEM	-	High Resolution Transmission Electron Microscopy
RE	-	Rare Earth
M	-	Modifier
CR	-	Cross Relaxation
GSA	-	Ground State Absorption
ESA	-	Excited State Absorption
ET	-	Energy Transfer

NPs	-	Nanoparticles
EDFA	-	Erbium Doped Fiber Amplifier
SPR	-	Surface Plasmon Resonance
NDT	-	Non Destructive Test
FWHM	-	Full Width at Half Maximum
DTA	-	Differential Thermal Analysis
UC	-	Upconversion
DC	-	Downconversion
HSTs	-	Hypersensitive Transitions
PL	-	Photoluminescence
SERs	-	Surface Enhanced Raman spectroscopy
NMR	-	Nuclear Magnetic Resonance
FTIR	-	Fourier Transform Infrared

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Over the last few eras, tellurite has been the high interest subject due to its capability as host for the development of application such as optical amplifier and solid state laser. Tellurite glass has some remarkable characteristic over other host material such as broad transparency window in visible and near IR (0.35-6 μm), high lanthanide ion solubility, high linear and non-linear refractive index (≥ 2), low melting point ($\sim 800^\circ\text{C}$), low phonon energy ($\sim 750\text{ cm}^{-1}$), high dielectric constant (~ 20) and very good stability [1].

Recently, ZrF_4 based fluoride glass also has attracts many researchers' attentions due to its great properties of high solubility for rare earth ions, low linear refractive index and has long florescence lifetime of the excited electronic state [2]. Compared with tellurite, fluoride glass has lower phonon energy around 500 cm^{-1} because it has high ionic bond character [3]. But, fluoride glass shows poor water resistance, mechanical durability and thermal stability. In order to overcome this problem, oxyfluoride tellurite glass is produced by the combination of fluoride with oxide glass because oxide glass has better water resistance, mechanical durability

and thermal stability. Cheng, *et. al* [4]., reported that, oxyfluoride-tellurite glass exhibit unique properties such as high lanthanide solubility, wide transmission window and low phonon energy particularly suitable used as host material of rare-earth for waveguide amplifier and laser.

Additionally, the incorporation of easily polarized heavy metal oxides with tellurite glass will enhance polarizability of Te^{4+} ions in glass network [5]. According to previous work, the addition of MgO in the glass structure will enhance the chemical durability of the glass [6]. Moreover, the addition of modifiers will modify and increase non-bridging oxygen, at the same time open up the glass structure. Therefore, the substitution of MgO in the glass network would produce the stable tellurite glass [7]. In order to achieve stable tellurite glass with high chemical durability, MgO will be added as one of the component in this study glass system.

In current investigation, Er^{3+} doped tellurite glass or fluoride glass has been studied by many researchers due to its great optical properties. Among the rare earth ions, Er^{3+} ion gets more attention due to its energy level structure that has been used in variety of glasses for application in solid-state lasers and optical amplifiers. It was reported that Er^{3+} doped oxyfluoride-tellurite glasses containing high concentration of ZnF_2 presented low density, long ${}^4\text{I}_{13/2}$ level lifetime, low OH^- ions concentration and wider transparency window. In comparison, the oxide tellurite glasses exhibits emission cross section spectra of ${}^4\text{I}_{13/2}$ - ${}^4\text{I}_{15/2}$ transition were quenched with a higher concentration of ZnF_2 [8]. In this study, it is expected that the presence of ZrF_4 in Er^{3+} doped oxyfluoride-tellurite glass will give better properties than other glasses due to the low phonon energy of ZrF_4 [8].

A lot of modification and work have been done in order to increase the luminescence in RE doped glass. Presently, the embedment of metallic nanoparticles (NPs) into glass matrices is the best approach to enhance the luminescence. The rare earth (Er^{3+} ion) is certified as dopant, while metallic nanoparticles (Au or Ag NPs) are react as stimulating agent to enhance the optical properties (absorption and

emission) [9]. The presence of metallic nanoparticles inside the glass host will change the glass matrix environment and can be optimized the spectroscopic properties of Er^{3+} ions including the change of chemical bonding in glass network and optical properties [10]. The luminescence intensity of RE strongly depends on the local electric field between the RE and NPs and subsequent energy transfer (ET) mechanism [9].

In order to understand the optical properties of the Er^{3+} doped oxyfluoride-tellurite glass embedded with Ag NPs, the glass will be characterized using X-Ray Diffractometer, High Resolution Transmission Electron Microscopy, UV-Vis-NIR spectrometer and Photoluminescence spectrometer. The optical energy band gap, refractive index, fluorescence branching ratios, thermal parameter, Judd-ofelt intensity parameter, spontaneous radiative transition probabilities and lifetimes were calculated to further evaluate the luminescence characteristic of the Er^{3+} doped zirconium oxyfluoride-tellurite glass embedded with Ag NPs.

1.2 Problem statement

Recently, the upconversion and downconversion of infrared light to visible light by various rare earth doped glass ions have widely been studied due to the capability in the field of photonics [11]. Generally, glass host with low phonon energy could be ideal for doping Er^{3+} ion due to the reducing of multiphonon de-excitation and enhancement on the quantum efficiency of luminescent transition [12]. Therefore, much effort has been spent on fluoride glass owing to their lower phonon energy [11]. However, fluoride glass frequently exhibits very poor chemical stability and mechanical durability [11]. On the other hand, oxide glass has better chemical stability and mechanical durability but unfortunately their higher phonon energy will limit their applications. Therefore in this study, the combination of fluoride glass with oxide glass will be developed to overcome this problem, it is

called oxyfluoride glass. In this study, the concentration of MgO is fixed at 10 mol% , which is similar concentration as other previous study [13–16].

From previous literature, it was reported that the Er^{3+} -doped zinc oxyfluoride tellurite glass exhibits quenching emission cross section spectra at $1.5\mu\text{m}$ with the increasing of ZnF_2 concentration [8]. However, in this study it is expected that Er^{3+} -doped zirconium oxyfluoride tellurite glass embedded with Ag NPs will get the enhancement of emission cross section spectra with the higher concentration of ZrF_4 . It is known that, the introduction of metallic NPs and RE ions in glass host exhibit higher potential on the enhancement of glass luminescence [17]. Additionally, since there are only few studies on these glasses and it is lack of information on the influence of Ag NPs and Er^{3+} ion on the oxyfluoride tellurite glass as shown in Table 1.1. Therefore, it is the aim of this research to provide more information on the physical and optical analysis of erbium doped zirconium oxyfluoride tellurite glass embedded with Ag NPs

1.3 Objective

The objectives of this study are:

- i. To prepare the oxyfluoride tellurite glass samples with different concentration of ZrF_4 , Er^{3+} ion and AgCl by melt quenching technique.
- ii. To determine the amorphous nature of the glass and verify the presence of Ag NPs.
- iii. To determine the influence of ZrF_4 , Er^{3+} ion and Ag NPs concentration on the optical properties of oxyfluoride tellurite glass.

Table 1.1: The previous study on Oxyfluoride tellurite glass.

Year.	Sample glass	Charecterization														
		Thermal properties			Absorption properties				Luminescene properties		Judd-Ofelt analysis ($^4S_{3/2}$ - $^4I_{15/2}$)				Structural properties	
		Spectra	T _g (°C)	T _c (°C)	ΔT (°C)	Spectra	E _{opt} (eV)	ΔE (eV)	n	Up	Down	Ω ₂	β	A	T (ms)	Raman
2003	TeO ₂ -ZnO - ZnF ₂ -Er ₂ O ₃ - Na ₂ CO ₃ - [18]		-	-	-	2 peak			-	-	2 peak (infrared)	-	-	-	-	3 band
2005	TeO ₂ -WO ₃ -ZnF ₂ [19]		339	493	154	-	2.69	0.12	-	-	-	-	-	-	-	-
2011	TeO ₂ -GeO ₂ -PbF ₂ -BaF ₂ -Er ₂ O ₃ [11]		503	646	143	8 peak	-	-	-	6 peak (red, green)	-	-	-	-	-	3 peak
2011	TeO ₂ - ZnF- ZnO- Er ₂ O ₃ [8]		302	488	126	11 peak	-	-	2.07	5 peak (red, green)	2 Peak (infrared)	4.40	-	-	8.80	6 peak
2013	TeO ₂ -ZnO- ZnF ₂ - Er ₂ O ₃ [81]	-	-	-	-	10 peak	-	-	2.002	3 peak (red, green)	2 peak (infrared)	4.71	67.3	3430.3	0.29	-
2017	TeO ₂ -P ₂ O ₅ - ZnO-PbF ₂ - MgO- Er ₂ O ₃ [20]	-	-	-	-	10 peak	-	-	2.91	10 peak	-	4.51	-	-	0.41	-

1.4 Scope of Study

Preparation of oxyfluoride tellurite glass by melt-quenching technique in four glass series of composition,

- Series 1: $(90-x)\text{TeO}_2-10\text{MgO}-(x)\text{ZrF}_4$, where $0 \leq x \leq 6$ in mol%.
- Series 2: $(84-y)\text{TeO}_2-10\text{MgO}-6\text{ZrF}_4-(y)\text{Er}_2\text{O}_3$, where $0 \leq y \leq 2$ in mol%
- Series 3: $(88.5-z)\text{TeO}_2-10\text{MgO}-(z)\text{ZrF}_4-1.5\text{Er}_2\text{O}_3$, where $0 \leq z \leq 6$ in mol%
- Series 4: $(82.5-w)\text{TeO}_2-10\text{MgO}-6\text{ZrF}_4-1.5\text{Er}_2\text{O}_3-(w)\text{AgCl}$, where $0 \leq w \leq 0.8$ in mol%.

The amorphous characteristic is confirmed using X-ray Diffraction spectroscopy (XRD) and the presence of Ag NPs in glass system is observed by High Resolution Transmission Electron Microscopy (HRTEM).

The optical properties of glass was determined by UV-Vis NIR and Photoluminescence spectroscopy in term of absorption coefficient, optical energy band gap, Urbach energy band gap, refractive index, Judd Ofelt intensity parameter, lifetime decay, Quality factor and stimulated emission cross section area.

1.5 Significance of study

Presently, the development of upconversion solid state laser has drawn many attentions in optical material sciences. The low phonon energy and large refractive index of oxyfluoride tellurite glass is the key to improving the fluorescence emission compare to other oxides and fluorides host. Low phonon energy of glass will reduced

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