SYNTHESIS AND CHARACTERIZATIONS OF DYSPROSIUM DOPED ZINC-SODIUM-TELLURITE GLASS

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To

my parents and siblings, whose sacrifice, dream, support and encouragement
lead to achieve my present educational level.
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ALHAMDULIILLAHI RABBIL ALAMIIN.
ABSTRACT

Rare earth ions (REIs) doped binary and ternary tellurite glass systems are attractive because of several technological applications. Transparent tellurite glasses can be achieved by combining the vitrified tellurium oxide (TeO$_2$) host with various modifier oxides of Zinc (ZnO), Sodium (Na$_2$O), Silicon (SiO$_2$), etc. over a wide composition range. Tellurite system is wellknown for large intake of REIs, excellent optical properties and low phonon energy cutoff. Determining the influence of dysprosium (Dy$^{3+}$) ions doping on the improvement of physical, structural and optical properties of tellurite glasses is the main focus of this research. A series of Dy$^{3+}$ ions doped zinc-sodium-tellurite glass having composition of (65-x)TeO$_2$-25ZnO-10Na$_2$O-xDy$_2$O$_3$ ($0 \leq x \leq 2.5$ mol\%) are prepared using melt-quenching method. Synthesized samples are characterized at room temperature via different analytical techniques. X-ray diffraction pattern verified the amorphous nature of the synthesized glass samples in the absence of any sharp crystalization peaks together with the presence of a broad hump between 25$^\circ$-35$^\circ$ diffraction angle. Differential thermal analysis revealed good thermal stability of the glass system in the range of 120-206 $^\circ$C and Hruby’s parameter between 0.47-1.33. Dy$^{3+}$ ions concentration dependent density and molar volume of the glass system is found vary in the range of 5.334 gcm$^{-3}$ - 5.366 gcm$^{-3}$ and 24.425 cm$^3$mol$^{-1}$ - 25.273 cm$^3$mol$^{-1}$, respectively. Fourier transformed infrared spectra exhibited bonding vibrations at the wavenumber of 590-615 cm$^{-1}$ and 772-817 cm$^{-1}$ which are assigned to [TeO$_4$] and [TeO$_3$] glass network structural units, respectively. Ultraviolet-Visible-Near-Infrared (UV-Vis-NIR) spectra displayed seven absorption peaks centred at 450, 752, 801, 1095, 1281, and 1687 nm which are allocated to the transitions from the ground level to the excited levels (such as $^4$F$_{9/2}$, $^6$F$_{3/2}$, $^6$F$_{5/2}$, $^6$F$_{7/2}$, $^6$H$_{7/2}$, $^6$H$_{11/2}$, and $^6$H$_{15/2}$) of Dy$^{3+}$ ions, respectively. The Dy$^{3+}$ ions contents dependent UV-Vis absorption edge data is used to calculate various optical properties of the glass. Indirect optical band gap is decreased from 2.67-2.30 eV and the Urbach energy is increased from 0.265-0.421 eV with increasing concentration of Dy$^{3+}$ ions. This indicated the enhancement of glass compactness and structural change mediated via non-bridging oxygen atoms in the network. Room temperature photoluminescence (PL) spectra showed three significant peaks centred at 497, 588, and 675 nm, which are attributed to the transitions from $^3$F$_{9/2}$ excited state to the $^6$H$_{11/2}$, $^6$H$_{13/2}$, and $^6$H$_{15/2}$ states of Dy$^{3+}$ ions, respectively. Highest PL intensity enhancement of 1.54 and 1.63 for yellow and red band, respectively is obtained for glass samples with 0.8 mol% Dy$^{3+}$ ions. The blue band of the sample with 1.2 mol% Dy$^{3+}$ ions revealed 1.46 times PL enhancement. This enhancement is ascribed to the excited state absorption and cross-relaxation processes. Overall, it is demonstrated that the physical, structural, thermal, and optical properties of the tellurite glass is improved due to the incorporation of Dy$^{3+}$ ions in the host matrix. Present optimized glass composition may be potential for the development of solid-state lasers and other photonic devices.
ABSTRAK

Sistem kaca telurit binari dan ternari dop ion nadir bumi atau Rare Earth Ions (REIs) adalah menarik berikutan beberapa aplikasi teknologi. Kaca telurit telus boleh dihasilkan dengan menggabungkan perumah kekaca telurium oksida (TeO₂) dengan pelbagai oksida pengubahsuai Zink (ZnO), Natrium (Na₂O), Silikon (SiO₂), dan lain-lain dalam jual komposisi yang luas. Sistem Telurit diketahui umum kerana pengambilan REI yang tinggi, ciri optik yang sangat baik dan penggalan tenaga fonon rendah. Menentukan pengaruh pengedopan ion disprosium (Dy³⁺) terhadap peningkatan ciri fizikal, struktur dan optik kaca telurit ialah fokus utama kajian ini.

Satu siri kaca zink-natrium-telurit dop ion Dy³⁺ dengan komposisi (65-x) TeO₂-25ZnO-10Na₂O-xDy₂O₃ (0 ≤ x ≤ 2.5 mol%) disediakan mengikut kaedah leburan-pelindapkejutan. Sampel disintesis dicirikan pada suhu bilik melalui teknik analisis berbeza. Pola pembelauan sinar-X mengesahkan sifat amorfus sampel kaca disintesis tanpa sebarang puncak penghabluran tajam, bersama-sama dengan kehadiran bonggol lebar dengan sudut pembelauan antara 25°-35°. Analisis terma berbeza mendahului kestabilan terma sistem kaca yang baik pada julat 120-206°C dan parameter Hruby antara 0.47-1.33. Ketumpatan bersandarkan kepekatan ion Dy³⁺ dan isi padu molar sistem kaca itu didapat berbeza-beza, masing-masing pada julat 5.334 g cm⁻³-5.366 g cm⁻³ dan 24.425 cm³ mol⁻¹-25.273 cm³ mol⁻¹. Spektrum inframerah terjelma Fourier menunjukkan getaran ikatan pada nombor gelombang 590-615 cm⁻¹ dan 772-817 cm⁻¹ yang diberikan, kepada unit struktur rangkaian kaca [TeO₄] dan [TeO₃]. Spektrum Ultraviolet-Visible -Near-Infrared (UV-Vis-NIR) memaparkan tujuh puncak penyerapan berpusat di 450, 752, 801, 901, 1095, 1281, dan 1687 nm yang diperuntukkan kepada peralihan dari aras bawah ke aras teruja (seperti ⁴F₉/₂, ⁶F₅/₂, ⁶F₇/₂, ⁶H₇/₂, ⁶F₁₁/₂, dan ⁶H₁₁/₂) ion Dy³⁺, masing-masing. Data tepi penyerapan UV-Vis bersandarkan kepejal kandungan ion Dy³⁺ digunakan untuk mengira pelbagai ciri optik kaca. Jurang jalur optik tidak langsung menurun daripada 2.67-2.30 eV dan tenaga Urbach bertambah daripada 0.265-0.421 eV dengan peningkatan kepejal kandungan ion Dy³⁺. Ini menunjukkan peningkatan kepadatan kaca dan perubahan struktur melalui pengantaraan atom oksigen bukan penitian dalam rangkaian. Spektrum kefotopendarcahayaan (PL) suhu bilik menunjukkan tiga puncak yang ketara berpusat di 497, 588, dan 675 nm, yang disebabkan oleh peralihan dari keadaan teruja ⁴F₉/₂ kepada keadaan ⁶H₁₁/₂, ⁶H₁₃/₂, dan ⁶H₁₅/₂ ion Dy³⁺, masing-masing. Peningkatan intensiti PL tertinggi pada 1.54 dan 1.63 untuk jalur kuning dan merah, masing-masing diperoleh dengan sampel kaca pada 0.8mol% ion Dy³⁺. Jalur biru sampel dengan 1.2mol% ion Dy³⁺ mendedahkan 1.46 kali peningkatan PL. Peningkatan ini dianggap berpunca daripada proses penyeraian keadaan teruja dan pengenduran silang. Secara keseluruhan, didapati bahawa sifat-sifat fizikal, struktur dan optik kaca telurit bertambah baik disebabkan oleh penggabungan ion Dy³⁺ dalam matriks perumah. Komposisi kaca teroptimum sekarang mungkin berpotensi untuk pembangunan laser keadaan pepejal dan peranti fotonik lain.
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<td>BS</td>
<td>Beam Splitter</td>
</tr>
<tr>
<td>BOs</td>
<td>Bridging Oxygens</td>
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<tr>
<td>CN</td>
<td>Coordination Number</td>
</tr>
<tr>
<td>CR</td>
<td>Cross Relaxation</td>
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<tr>
<td>DC</td>
<td>Down Conversion</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analyser</td>
</tr>
<tr>
<td>ET</td>
<td>Energy Transfer</td>
</tr>
<tr>
<td>ENDO</td>
<td>Endothermic</td>
</tr>
<tr>
<td>EXO</td>
<td>Exothermic</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive Electron Microscope</td>
</tr>
<tr>
<td>FIR</td>
<td>Far Infrared</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal Closed-Packed</td>
</tr>
<tr>
<td>HSTs</td>
<td>High Sensitive Transitions</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MIR</td>
<td>Mid Infrared</td>
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<tr>
<td>NBO</td>
<td>Nonbridging Oxygen</td>
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<tr>
<td>NIR</td>
<td>Near Infrared</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>NR</td>
<td>Nonradiative</td>
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<td>PL</td>
<td>Photoluminescence</td>
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<td>RE</td>
<td>Rear Earth</td>
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<tr>
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<tr>
<td>tbp</td>
<td>Trigonal Bipyramid</td>
</tr>
<tr>
<td>tp</td>
<td>Trigonal Pyramid</td>
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<tr>
<td>UP</td>
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<tr>
<td>UV-Vis-NIR</td>
<td>Ultraviolet-Visible-Near Infrared</td>
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VB - Valence Band
XRD - X-Ray Diffraction
LIST OF SYMBOLS

$2\theta$ - Diffraction angle

$\alpha_e$ - Polarizability

$\alpha(\nu)$ - Absorption coefficient

$\bar{A}$ - Angstrom

$Ax$ - Axial

°C - Degrees centigrade

$D$ - Crystal lattice planar spacing

$\Delta E$ - Urbach energy

$E_c$ - Conduction band energy

$E_{opt}$ - Optical band gap energy

$E_q$ - Equatorial

$E_v$ - Valence band energy

$H$ - Hruby parameter

$H\nu$ - Photon energy

$I_{\text{sample}(q)}$ - Luminescence intensity of other glass samples

$I_{\text{reference}}$ - Luminescence intensity of glass sample with 0.4 mol% of Dy$^{3+}$ ion

$K$ - Kelvin

$KBr$ - Potassium bromide

$Ln$ - Lanthanide

$M_{av}$ - Average molecular weight

$N$ - Refractive index of glass

$N_A$ - Avogadro’s number

$N(E_c)$ - Density of states at the conduction band

$N(E_v)$ - Density of states at the valence band

$n_r$ - Order of reflection
\[ \Theta \] - Angle of incidence
\[ \sigma_0 \] - Conductivity
\[ \Lambda \] - Wavelength
\[ \rho \] - Glass density
\[ \rho_a \] - Air density
\[ \rho_l \] - Density of immersion liquid
\[ R \] - Optical transition index
\[ R_m \] - Molar refractivity
\[ T \] - Temperature
\[ T_c \] - Glass crystallization temperature
\[ T_g \] - Glass transition temperature
\[ T_m \] - Glass melting temperature
\[ \Delta T_s \] - Glass thermal stability
\[ T_x \] - Glass onset crystallization temperature
\[ N \] - Frequency
\[ V_m \] - Molar volume
\[ W_a \] - Weight of glass in air
\[ W_l \] - Weight of glass in immersion liquid
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CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter gives a brief background on the development of glass research especially tellurite glass, aims towards potential application in solid state physics and other optical devices. Also it introduce the problem statement, objectives, scope of the study and significance of the research.

1.2 Research Background

In the realm of controlled modified and enhance properties of rare earth (RE) doped glass for various practical application, achieving this, is a quest which cannot be over-emphasised. Having special properties in relation to plastic or metal, makes glass a unique material. Some of this properties makes it to be increasingly used as good host for laser, based on RE and metal ionic transitions. Tellurite based glasses are regarded as excellent materials for the above purpose (host for lasing ions). Conversely, tellurium dioxide (TeO$_2$) as a pure oxide, manifests itself as simply a restrictive glass-former, which needs a special fast-quenching technique to vitrify [1]. Vitrifying TeO$_2$ using traditional process encountered difficulty, achieving high transparent tellurite glasses are done by hosting other oxides like transition metal oxides: Zinc oxide (ZnO), alkaline oxides: sodium oxide (Na$_2$O) and alkaline earth
oxide: magnesium oxide (MgO) devoid of adding any conventional glass former such as P_{2}O_{5}, SiO_{2} and B_{2}O_{3} [2]. Physical, structural and optical parameters of rare earth ions (REIs) doped glasses have been extensively examined owing to their prospective uses in fabrication of innovative optical devices. As uncover via optical studies, the radiative behaviour of the REIs in glasses is intensely influenced by the host matrix, also, can be improved through suitable selection of network former together with network modifier ion [3].

Over the years RE predominantly Dy^{3+}, Eu^{3+}, Sm^{3+}, Er^{3+}, and Pr^{3+}, doped glasses shown to be eye-catching in emerging countless active optical devices [4]. Numerous researches worked on Dysprosium (Dy^{3+}) ion owing to it prospect in fabrication of various types of light emitting materials for blue, yellow and red luminescence conforming to transitions of ^4F_{9/2}→^6H_{J}, (J=15/2, 13/2, 11/2) respectively [5, 6].

1.3 Motivation of the Study

Owing to its optical absorption, glass displays certain colours, which have been intensively utilised in the areas of optical fibre communications and optical switching [7]. A number of compositions of glasses are being synthesised, with enormous properties by means of different families of the periodic table such as oxide, chalcogenide, halide etc. [1].

Oxide glasses are synthesised from a number of oxides commonly SiO_{2}, P_{2}O_{5}, B_{2}O_{3}, GeO_{2}, TeO_{2} etc. One of the advantages of oxide glasses is that they can be simply prepared by melt quench technique, with challenging properties paralleled to chalcogenide glasses [1].

Among the oxide glasses one of the most proper hosts for doping RE element are thought to be tellurite glasses, making it to have growing attention due to its unique physical properties. In latest years, significant consideration has been given to
solid materials doped with RE owing to their prospective usage as colour displays, glowing and optoelectronic devices [8, 9].

The REIs energy levels decide the lasing properties of RE doped systems and are subjective to glass former matrix [10]. The optical characteristics of zinc fluorophosphate glasses doped with Dy$^{3+}$ ions were described [11]. Sasi kumar et al, 2013 put forward the absorption and PL behaviour of Dy$^{3+}$-doped heavy metal borate glasses-effect of modifier oxides [12]. Swapna, et al, 2013 explored the absorption and luminescence properties of Dy$^{3+}$-doped zinc alumino bismuth borate glasses for laser devices so also white light emitting diodes (LEDs) [13]. Balakrishna, et al, 2012 considered structural and PL characteristics of Dy$^{3+}$ doped different modifier oxide-based lithium borate glasses [14].

1.4 Problem Statement

There have been some limitations of REIs doped tellurite glass due to low absorption and emission cross-section (measure for the probability of absorption and emission occurrence) in spite of various distinct features [15]. However, the low stability, low absorption and emission as well as structural strength of tellurite glass needs improvement. In this regard, optimum composition of tellurite glass system is not been explored yet [16]. Discovering new prospective lasing transition and to raise the component of lasing transitions, REIs doped glass has been painstakingly investigated in diverse glass base, so also in particular their optical behaviour [17].

Much concern on tellurite glasses are motivated by their use in several industrial usages specifically in laser glass technology [18]. Dy$^{3+}$ ions are doped inside the tellurite glass system because of their sharp emission line in the IR and visible region. Moreover, tellurite glass is a good host that produce enhanced absorption and emission properties of rare earth suitable for laser application [19]. Yet most of the report are partly on tellurite glasses doped with Eu$^{3+}$, Nd$^{3+}$ and Er$^{3+}$. 
Not much studies have been reported on the Dy\(^{3+}\) doped zinc-sodium-tellurite glasses and also the optimum concentration with this rare earth ion is not develop yet.

In this study, it shown synthesis and characterization of zinc sodium tellurite glass doped with Dy\(^{3+}\). Also low transition temperature and presence of hygroscopic properties limit the application of phosphate and borate glasses in comparism to zinc sodium tellurite glass system [20]. The comprehensive information on the structures, thermal and optical properties of Dy\(^{3+}\) doped zinc-sodium-tellurite glasses are still deficient [21]. Therefore structural thermal and optical properties of the glass system under study need to be investigated.

1.5 Objectives of the Study

The objective are listed below:

i. To synthesize Dy\(^{3+}\) ions doped zinc sodium tellurite glass with optimum composition.

ii. To characterize the prepared Dy\(^{3+}\)-doped zinc-sodium tellurite glass systems for their physical, structural and thermal properties.

iii. To determine the influence of Dy\(^{3+}\) ions on the optical properties of the synthesized glass systems.

1.6 Scope of the Study

Owing to the utmost result of TeO\(_2\)-ZnO-Na\(_2\)O glass system as put forward by [22-24] leading to the decision of (65-x)TeO\(_2\)-25ZnO-10Na\(_2\)O-xDy\(_2\)O\(_3\) as the preferred composition for this study. As reported heavy metal oxide (like ZnO) has been used as a favourable constituent materials aimed for tellurite- based fibres [25] The study of structural, thermal and optical properties of glasses is crucial to give a
clear understanding of the growth and thermal stability which is fundamental to prepare a glass with optimal properties.

i. The amorphous nature of the glass was confirmed using XRD.

ii. Further study on structural behaviour as regard to bonding vibrations of the glasses are demonstrated by FTIR spectroscopy.

iii. The thermal properties of glass including the crystallization temperature, glass transition temperature, glass stability and Hruby’s parameter are determined by using differential thermal analysis (DTA).

iv. Meanwhile, the optical properties of glass are studied by using UV-Vis-NIR and PL spectroscopy.

The thermal, optical and structural studies are vital to select suitable glass with optimized parameters to be used in various optical-based devices [26]. This study gives an in-depth on aforementioned spectroscopic properties of zinc-sodium tellurite glass system doped with Dy$^{3+}$ ions.

### 1.7 Significance of the Study

The search for profitable and industrial down-converted lasing glass is eternally swelling. Due to the demand for several industrial applications, more study on glass materials is vital. There is need to relate in many aspects such as physical, optical, structural and other properties with precise and superior characteristics manufactured glassy materials.
This dissertation will allows us to synthesize a glass composition by doping Dy\(^{3+}\) ion, The improvement in the structural, optical, thermal and physical properties will be understood by systematic characterizations.

Thermal stability will be improved.

The enhancement of the absorption and emission properties of the glass will be useful for many optical devices.

The mechanism of optical enhancement and structural change due to the influence of Dy\(^{3+}\) ion will be understood clearly.

1.8 Thesis Outline

Chapter one comprises the research background of tellurite glass, discusses the importance of the samples to be prepared in relation to its optical, photoluminescence, thermal and structural properties. Zinc-sodium-tellurite glass doped with dysprosium is to present a glass material with potential in optical devices. The set objectives to be achieved are also enumerated.

Chapter two, it offered wide-ranging explanation concerning of glass structure and behaviour of Zinc, Sodium as modifiers to tellurite systems with the influence of dysprosium as RE dopant. The physical, optical, thermal and structural properties likewise will be reviewed.

Chapter three, it encompasses the procedural steps used in the glass preparation, techniques employed in investigating the various spectroscopic measurements with the physical properties are well detailed.
REFERENCES

1. Rose Leena, T.: *Synthesis and Characterization of Tellurium Oxide Glasses for Photonic Applications* Ph.D. Thesis International School of Photonics, Cochin University of Science and Technology; 2013.


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