

PHYSICAL, STRUCTURAL AND OPTICAL PROPERTIES OF TERBIUM
DOPED ZINC PHOSPHATE GLASSES EMBEDDED WITH COPPER OXIDE
NANOPARTICLES

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy (Physics)

Faculty of Science
Universiti Teknologi Malaysia

JANUARY 2019

DEDICATION

.....dedicated to my lovely family members:

My beloved father ♥ (Syed Yaacob Bin Syed Ok)

My dearest caring mother ♥ (Sharifah Sabiha Binti Shah Ajam)

My dear sister ♥ (Syariffah Nuraqilah Binti Syed Yaacob)

My dear twin sister ♥ (Syariffah Nuratiqah Binti Syed Yaacob)

My dear younger sister ♥ (Syariffah Nuradilah Binti Syed Yaacob)

For their unconditional love, motivation and support

ACKNOWLEDGEMENT

Alhamdulillah, I am so grateful to Allah Almighty on His Merciful and all the compassionate and blessing for giving me strength courage and patience to complete this research. First and foremost I would like to express my sincere gratitude to my dedicated supervisors Prof. Dr Md.Rahim Sahar for encouragement, guidance critics and supports. I also would like to acknowledge the supervision of my co-supervisor Dr. Ezza Syuhada Sazali for their continuous support during all these years. Their taught experience and guidance were really appreciated. It would not have been possible to write this master thesis without the support, help and the prayers of my parents (Syed Yaacob Bin Syed Ok and Sharifah Sabiha Binti Shah Ajam). Also, I would like to thank my family for their endless love and support.

I would like to express my immense gratitude to the rest of people who contribute to my research work: all the lectures who has taught me, Mr Mohd Jaafar, Mr. Abd Rahman and Mdm Anisah. I would like to show gratitude to my seniors, Dr. Zahra Ashur and Dr. Siti Maisarah Aziz for the advice and discussion contributing to my research. Last but not least my sincere appreciation extends to Nur Amanina, Nur Amalina, Mohd Faiz, Nur Liyana Siti Aisyah, Khalijah, Khamisah, Puzi Anigrahawati, Nur Liyana, Zainatul Izzah, Syazlin and others who have provided assistance for my research. Their view and opinion are highly appreciated.

ABSTRACT

This thesis reports the modification of zinc phosphate glass properties as the concentration of terbium ion (Tb^{3+}) and copper oxide nanoparticles (CuO NPs) are varied. Three series of glass with composition of $(100-x) P_2O_5-xZnO$ with $30 < x < 80$ mol% in Series 1, $(60-x) P_2O_5-40ZnO-xTb_2O_3$, with $0.5 < x < 3.0$ mol % in Series 2 and $(57-x) P_2O_5-40ZnO-3Tb_2O_3-xCuO$ with $0.5 < x < 2.0$ mol% in Series 3 had been prepared by melt quenching technique. It was observed that the glass samples in Series 1 and Series 2 were colourless and the glasses in Series 3 were blue in colour. The existences of the broad humps in X-ray diffraction (XRD) pattern clarify the amorphous nature of the glasses. The energy dispersive x-ray analysis (EDAX) detected the presence of the required elements in the glass composition. The presence of CuO NPs with the size of 0.11 nm in the glass matrix has been verified using high-resolution transmission electron microscope (HRTEM). The thermal properties and glass stability were determined using differential thermal analyser (DTA). The sample exhibited glass stability up to 287 °C. The glass density (ρ), molar volume (V_m) and ionic packing density (V_t) were found to be in the range of (2.86-3.60) g cm⁻³, (25.90-43.28) cm³ mol⁻¹ and (0.582-0.741) respectively. The vibrational spectroscopy were analysed using Fourier transform infrared spectroscopy (FTIR) and ultraviolet-visible spectroscopy. Three major infrared absorption peak were found around 550 cm⁻¹, 794 cm⁻¹, 1165 cm⁻¹ and 1264 cm⁻¹ due to the vibration of (P-O) bond, stretching vibration of (P-O-P) bond, stretching vibrations (P=O) and asymmetric stretching vibration (P-O) bond. Surface plasmons resonance peak of CuO NPs was detected at 375 nm. The absorption spectra displayed five prominent bands owned to Tb^{3+} ion at 374 nm, 487 nm, 1878 nm, 1980 nm and 2231 nm. All these bands corresponded to ${}^7F_6 \rightarrow {}^5D_3$, ${}^7F_6 \rightarrow {}^5D_4$, ${}^7F_6 \rightarrow {}^7F_{1,2,3}$ and ${}^7F_6 \rightarrow {}^7F_3$ transitions respectively. The optical energy band gap and Urbach energy were in the range of (2.95-4.84 eV) and (0.19-0.63 eV) respectively. Meanwhile, the refractive index, molar refractivity and electronic polarizability had been calculated in the range of (2.00-2.40), (16.42-28.80) and (0.65-1.11) Å³. The emissions of the glass with Tb^{3+} ion were determined using photoluminescence spectroscopy. The glass samples were excited at 378 nm excitation wavelength and the emission spectra were found to consist of several emission bands at 413 nm, 435 nm, 457 nm, 488 nm, 540 nm 585 nm and 620 nm due to electronic transitions from ${}^5D_3 \rightarrow {}^7F_5$, ${}^5D_3 \rightarrow {}^7F_4$, ${}^5D_3 \rightarrow {}^7F_3$, ${}^5D_4 \rightarrow {}^7F_6$, ${}^5D_4 \rightarrow {}^7F_5$, ${}^5D_4 \rightarrow {}^7F_3$ and ${}^5D_4 \rightarrow {}^7F_5$ respectively. The presence of CuO NPs gave remarkable effects on the luminescent intensity. However, it was observed that the emission bands possess significant quenching effect at the higher concentration of CuO NPs.

ABSTRAK

Tesis ini melaporkan sifat kaca zink fosfat apabila kepekatan ion terbium (Tb^{3+}) dan nanozarah kuprum oksida (CuO NPs) diubahsuai. Tiga siri kaca zink fosfat berkomposisi $(100-x) P_2O_5-xZnO$ dengan $30 < x < 80$ mol% bagi Siri 1, $(60-x) P_2O_5-40ZnO-xTb_2O_3$ dengan $0.5 < x < 3.0$ mol% bagi Siri 2 dan $(57-x)P_2O_5-40ZnO-3Tb_2O_3-xCuO$ dengan $0.5 < x < 2.0$ mol% bagi Siri 3 telah disediakan menggunakan teknik pelindapan leburan. Kaca Siri 1 dan Siri 2 tidak berwarna manakala kaca Siri 3 berwarna biru. Kewujudan puncak lebar pada corak pembelauan sinar-x membuktikan kaca dalam keadaan amorfus. Analisis sinar-x serakan tenaga (EDAX) mengesan kehadiran unsur-unsur sebenar dalam komposisi kaca. Kehadiran nanozarah kuprum oksida (CuO NPs) yang bersaiz 0.11 nm telah dibuktikan dengan menggunakan mikroskop electron penghantaran beresolusi tinggi (HRTEM). Sifat dan kestabilan terma kaca telah ditentukan menggunakan penganalisis terma pembezaan (DTA). Kestabilan terma kaca sehingga 287 °C boleh dicapai. Ketumpatan kaca (ρ), isipadu molar (V_m) dan ketumpatan padatan ionik (V_t) didapati masing-masing berada dalam julat (2.86-3.60) g cm⁻³, (25.90-43.28) cm³ mol⁻¹ dan (0.582-0.741). Spektroskopi getaran kaca dianalisis menggunakan spektroskopi transformasi Fourier infra merah (FTIR) dan spektroskopi UV-Vis. Tiga puncak penyerapan infra-merah utama ditemui sekitar 550 cm⁻¹, 794 cm⁻¹, 1165 cm⁻¹ dan 1264 cm⁻¹ masing-masing disebabkan oleh getaran ikatan (P-O), getaran regangan ikatan (P-O-P), getaran regangan ikatan (P=O) dan getaran regangan tak simetri ikatan (P-O). Puncak resonans plasmons permukaan CuO NPs dikesan pada 375 nm. Spektrum penyerapan memaparkan lima jalur penyerapan ion Tb^{3+} iaitu pada 374 nm, 487 nm, 1878 nm, 1980 nm dan 2231 nm. Semua jalur penyerapan berdasarkan pada transisi $^7F_6 \rightarrow ^5D_3$, $^7F_6 \rightarrow ^5D_4$, $^7F_6 \rightarrow ^7F_{1,2,3}$ dan $^7F_6 \rightarrow ^7F_3$. Jurang tenaga optik dan tenaga Urbach ditemui masing-masing berada dalam julat (2.95-4.84 eV) dan (0.19-0.63 eV). Sementara itu, indeks biasan, pembiasan molar dan pengutuban elektronik telah dikira dan berada dalam julat (2.00-2.40), (16.42-28.80) dan (0.65-1.11) Å³. Pancaran dari kaca dengan ion Tb^{3+} ditentukan dengan menggunakan spektroskopi fotoluminesens. Sampel kaca diuja pada panjang gelombang 378 nm dan spektrum pancaran didapati terdiri daripada jalur pancaran yang berada pada 413 nm, 435 nm, 457 nm, 488 nm, 540 nm 585 nm dan 620 nm yang masing-masing mewakili peralihan $^5D_3 \rightarrow ^7F_5$, $^5D_3 \rightarrow ^7F_4$, $^5D_3 \rightarrow ^7F_3$, $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_3$ dan $^5D_4 \rightarrow ^7F_5$. Kehadiran CuO NPs memberi kesan yang luar biasa kepada keamatan pancaran. Walau bagaimanapun, semua puncak mengalami kesan pelindapan pada kepekatan CuO NP yang tinggi.

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LIST OF ABBREVIATIONS

E_{opt}^I	-	Indirect energy band gap
$h\nu$	-	Photon energy
ΔE	-	Urbach energy
BO	-	Bridging oxygen
NBOs	-	Non-Bridging oxygen
P_2O_5	-	Phosphate
ZnO	-	Zinc oxide
Tb_2O_3	-	Terbium Oxide
CuO NPs	-	Copper Oxide Nanoparticles
NPs	-	Nanoparticles
RE	-	Rare earth
UV	-	Ultraviolet
SPR	-	Surface plasmons resonance
NIR	-	Near Infrared Region
HRTEM	-	High Resolution Transmission Electron Microscope
EDX	-	Energy Dispersive Analysis X-Ray
DTA	-	Differential Thermal Analysis
FTIR	-	Fourier Transform Infrared

LIST OF SYMBOLS

E	-	Energy
ν	-	Wavenumber
n	-	Refractive index
δ	-	Bonding parameter
β	-	Nephelauxetic ratio
N	-	Avogadro's Numbers
V_m	-	Molar volume
V_t	-	Ionic packing density
x_i	-	Molar fraction
N	-	Ion concentration
R_m	-	Molar refraction
α_m	-	Electronic polarizability
2θ	-	Braggs angle
d	-	Interatomic spacing
T_c	-	Crystallization temperature
T_g	-	Glass Transition temperature
T_m	-	Melting temperature

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Glass is a non-crystalline material that has been used in various applications since ancient time. Its atomic is lack of periodic arrangement and can be formed by fast cooling from a melt into low temperature without crystallization [1]. The evolutions of glass development reflect the interest in glass technology. Recently glasses possessed growing interest in engineering materials for abundant application such as solid-state lasers, fiber amplifiers, and optical fibers. It can be used to study the influence of chemical environment on the physicals, structural and optical properties of the rare earth ions (RE). This is due to the flexible properties that can be tuned by compositional modifications. They are also easily fabricated and with even distribution of rare earth as a glass host. Besides that glass also own an exquisite features such as high chemical durability to withstand extreme environment [2]. Several techniques has been employed to prepare the glass such as sol-gel, melt quenching.

A lot of efforts have been devoted to studying various materials to form glass. Phosphate (P_2O_5) based glasses are considered suitable material for lasing action due to its unique properties [3]. It is due to the excellent properties of phosphate glass such as high thermal expansion, melt at low temperature, and possessed high ultraviolet (UV) and far infrared transmissions for optical data transmission [4]. Besides that, phosphate allows the introduction of the large concentration of RE without clustering. This significant behaviour gives impact on producing glass with highly effective pumping and exhibits efficient energy transfer from the RE [5]. The previous study reported that phosphate glass exhibits low chemical durability, which is due to the hygroscopic nature of phosphate glass. However, the inclusion of dopant ion such would improve and enhance their chemical durability [6]. The introduction of metal

oxide such as zinc oxide into the phosphate network promotes more non-bridging oxygen (NBOs) and substantially leads to polymerization of the phosphate glass network by forming P-O-Zn bond. As a result, the resistance of the aqueous water attack in the phosphate network can be increased. [7,8]

Intensive research on the developments of RE ion doped glass has gained new knowledge on developing a high performance optical active devices. The photoluminescence characteristic of RE ion such as Er^{3+} [9], Eu^{3+} [10], Tm^{3+} [11], Tb^{3+} [12], Pr^{3+} [13], Sm^{3+} [14] and Dy^{3+} [15] as luminescent materials has been established owing to their optical transition in the visible and near infrared region (NIR) [16]. In addition, RE ions have been chosen as dopant due to several factors. The shielding effect of $5s^2$ and $5p^6$ shells gives narrow band in excitation and emission spectra. Although RE ion doped into a different kind of host glass, the shielding effect remains their nature behaviour [17].

Among the trivalent RE ions, Tb^{3+} ions have created new interest due to its strong luminescent. The photoluminescence emission of Tb^{3+} lies in the blue and green region. Tb^{3+} possess a mild blue and intense green emission. In particular, the mild blue and intense green emission is produce at 542 nm due to radiative decay from $^5\text{D}_4$ excited states to $^7\text{F}_5$ ground states [18]. Fascinatingly glass doped with Tb^{3+} ion exhibits large energy band gap around 4.65eV [19,20]. However, the fluorescence quantum yield of Tb^{3+} is limiting their performance. At the emission of 378 nm, the intensity of Tb^{3+} increase then drops beyond a certain point of concentration due to the quenching effects. Generally, the quenching phenomenon is observed due to clustering of RE ion at a high concentration of more than 3.0 mol % of Tb^{3+} [21,22]. Consequently, the performance of the host matrix finally become inactive. In sequence to surmount of the quenching effect, the introduction of metallic NPs has been proposed to encounter the effect.

Presently the nano era development induces synthesis of new nanostructure materials with simple technique along with incredible properties and feasible application. The initiative of embedment of metallic NPs in RE-doped glass is known to enhance the luminescence efficiency [23]. The introduction of NPs in RE-doped glass explicitly develops new promising functional materials. The discoveries of the NPs doped with RE began when Malta reported the effect of Ag NPs Er^{3+} in fluoroborate glass. They revealed that the luminescence enhances for glass containing Eu^{3+} ion. The enhancement is due to the presence of small Ag NPs [24]. NPs exhibit localized surface plasmons resonance (LSPR) that generate strong local electric field assure the excitation transfer to the RE ion [25]. In particular, light interaction between RE ion incorporate with metal NPs perceived to overcome the quenching of RE through the energy transfer [26]. The incorporation of metallic NPs inside the glass host change the local environment triggered by the RE ions.

1.2 Problem Statement

The photoluminescence characteristics of rare earths doped into various kind of hosts have been extensively studied in the past due to its wide range of its application such as optical data storage and medical treatment [27]. These glasses recognized as fascinating materials due to the f-f transition lies on the visible and near-infrared (NIR) region [18]. The unique properties of lanthanide ions assigned them as luminescent indicator group for laser development [28]. Among all lanthanide ion, progressive research has been focus on producing green laser by Er^{3+} doped glass pumped with 0.8 μm laser diodes [29]. However, not many studies have been reported on the use of Tb^{3+} ions. In sequence, optimum concentration of Tb^{3+} doped zinc phosphate glass are important to emphasized in order to avoid from quenching and enhance stability [30]. Since there is lack of reports on these glass, it is therefore the aim of this study to give more information on the influence of Tb^{3+} on zinc phosphate glass.

The influence of metallic NPs on RE doped glass has been widely studied. These NPs contribute an enormous effect on enhancing the luminescence through

energy transfer. Till now most of the study has focus on the embedment of NPs such as Ag NPs [31] Au NPs [32] Fe NPs [33] Ni NPs [34] and Mn NPs [35]. Although continuous significant efforts has been devoted to study all those metallic NPs, yet the effect of CuO NPs on RE doped glass is not yet been explored. Hence it is a great of interest to study their roles on the doping glass. In this work, the effects of CuO NPs on the phosphate glass doped with Tb^{3+} ions will be studied in term of their physical, structural and optical behaviour along with the mechanism of the respective properties.

1.3 Objectives

In order to overcome the problem that has been stated in section 1.2 several objectives have been outlined in this research as follows:

- 1) To prepare three series of glass by melt quenching technique. The compositions are as below:
 - i. **Series 1**
(100-x) P₂O₅-xZnO where $30 \leq x \leq 80$ mol%
 - ii. **Series 2**
(60-y)P₂O₅-40ZnO -xTb₂O₃ where $0 \leq y \leq 3.0$ in mol% and
 - iii. **Series 3**
(57-z)P₂O₅-40ZnO-3.0Tb₂O₃-zCuO where $0 \leq z \leq 2.0$ mol%
- 2) To determine the amorphous nature of glass by X-Ray diffraction and the presence of NPs in the glass
- 3) To study the physical properties and the thermal parameter of the glass.
- 4) To determine the structural properties of the glass.
- 5) To study the optical properties of the glass

1.4 Scope of Study

This study is attempted to determine the properties of the glasses of three different series with different composition prepared by using melt quenching technique. The thermal parameters such as glass transition temperature (T_g) crystallization temperature (T_c) and melting temperature (T_m) along with the thermal stability in all composition are determined by using differential thermal analysis (DTA). The amorphous natures of the prepared glasses are examined by X-Ray diffraction. The existence of CuO NPs is verified using High Resolution Transmission Electron Microscope (HRTEM). Meanwhile the density is determined by using Archimedes Principle. The optical characteristic in term of their vibration features is determined by Fourier Transform Infrared Spectroscopy (FTIR). The study of absorption features, the optical energy band gap, Urbach energy refractive index and polarizability using UV-Vis NIR spectroscopy. The enhancement of emission and spectroscopic quality are accomplished by using Photoluminescence (PL) spectroscopy. Overall, the physicals, thermal and optical analysis are important to evaluate the glass properties in order to be used in various optical applications.

1.5 Significance of Study

The finding of efficient lasing glass with superior properties is ever demanding. The search for new glassy materials is important in order to meet the demands in glass industries to be used in various applications. Thus, the glass should possess particular and superior properties in many aspects such as physical, structural and optical properties. In this research, incorporation of CuO NPs in the glass matrix creates potential glass materials useful for non-linear photonic devices. A basic understanding underlying on the mechanism of CuO NPs doped with terbium zinc phosphate glass provides new gain insight on structural and optical properties. In addition, SPR exhibited by CuO NPs provides a new view of the Plasmon excitation efficiency on RE-doped glass. This research provides significant finding into extending of information regarding the production of new materials in order to develop new non-linearity photonic devices for widely used in solid-state application.

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