

SILVER NANOPARTICLE ENHANCED THE OPTICAL PROPERTIES OF THE
RARE EARTH DOPED MEGNESIUM ZINC SULFOPHOSPHATE GLASS

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I dedicated this thesis to my beloved father and mother for their support and encouragement.

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ABSTRACT

Magnesium-zinc-sulfophosphate (P_2O_5 -MgO-ZnSO₄) glasses being a prospective host for lasing active media require precise composition optimization and systematic characterization. A series of glass samples in the composition of $(60.0-x)P_2O_5$ -20.0MgO-20.0ZnSO₄-xRE₂O₃ ($0.0 \leq x \leq 2.0$ mol% and rare earth (RE) = Sm, Dy, and Er), $(59.5-y)P_2O_5$ -20.0MgO-20.0ZnSO₄-0.5RE₂O₃-yAgCl ($0.0 \leq y \leq 0.5$ mol% and RE = Sm and Dy) and $(59.5-z)P_2O_5$ -20.0MgO-20.0ZnSO₄-0.5Er₂O₃-zAgCl ($0.0 \leq z \leq 1.5$ mol%) were synthesized using melt-quenching technique. The samples were thoroughly characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FTIR), ultraviolet-visible (UV-Vis) absorption, photoluminescence (PL) and Raman spectroscopy. XRD verified the samples amorphous nature and TEM images manifested the nucleation of homogeneously distributed spherical silver (Ag) nanoparticles in the glass matrix. FTIR spectra revealed the bonding vibrations for P-O bonds, P-O-P linkages, and PO₂ units. There is no evidence in Raman spectra of RE (RE= Sm, Dy and Er) doped P_2O_5 -MgO-ZnSO₄ glasses to confirm the incorporation of the sulfate ions to the network formation. The absorption spectrum of RE (RE = Sm, Dy and Er) doped P_2O_5 -MgO-ZnSO₄ glasses with and without incorporation of Ag nanoparticles is originated from electronic transitions from the ground level to various excited levels belonging to the $4f^9$ electronic configuration of the RE ions. Absorption and emission spectra are used to evaluate the Judd-Ofelt (JO) intensity parameters and radiative transition probabilities, branching ratios and stimulated emission cross-sections of the three RE ion (RE = Sm, Dy, and Er) doped glass systems. The room temperature PL spectra of samarium-doped glass revealed four emission peaks centered at around 562, 599, 644, and 702 nm, which are assigned to the transitions from $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$, respectively. The PL spectra of dysprosium-doped glass displayed two prominent peaks at around 480 nm and 574 nm corresponding to the $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions, respectively and two weak peaks. Conversely, erbium-doped glass system exhibited two strong emission peaks centered at around 541 nm and 654 nm attributed to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions, respectively. All glass series containing Ag nanoparticles showed considerable emission intensity enhancement, which is attributed to the nanoparticle surface plasmon resonance mediated intensified local field effect in the proximity of RE ions. Overall properties of each glass series are demonstrated to be modified due to the embedment of Ag nanoparticles. Among all the glass series produced, the stimulated emission cross-section for $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition in erbium-doped glass system is discerned to be the highest.

ABSTRAK

Kaca magnesium-zink-sulfofosfat (P_2O_5 -MgO-ZnSO₄) sebagai satu hos prospektif bagi media aktif las memerlukan pengoptimuman komposisi yang persis dan pencirian yang sistematik. Satu siri kaca dengan komposisi $(60.0-x)P_2O_5$ -20.0MgO-20.0ZnSO₄- xRE_2O_3 ($0.0 \leq x \leq 2.0$ mol% dan nadir bumi (RE) = Sm, Dy, dan Er), $(59.5-y)P_2O_5$ -20.0MgO-20.0ZnSO₄-0.5RE₂O₃- $yAgCl$ ($0.0 \leq y \leq 0.5$ mol%) dan $(59.5-z)P_2O_5$ -20.0MgO-20.0ZnSO₄-0.5Er₂O₃- $zAgCl$ ($0.0 \leq z \leq 1.5$ mol%) telah disintesis menggunakan teknik lebur-lindap kejut. Sampel telah dicirikan secara terperinci dengan menggunakan pembelauan sinar-x (XRD), mikroskopi elektron penghantaran (TEM), spektroskopi infra merah jelmaan Fourier (FTIR), spektroskopi serapan ultraungu-nampak (UV-Vis), spektroskopi kefotopendarcahayaan (PL) dan spektroskopi Raman. XRD telah menentukan sifat amorfus sampel dan imej TEM telah menunjukkan penukleusan zarah nano perak (Ag) berbentuk sfera yang teragih secara homogen dalam matriks kaca. Spektrum FTIR memperlihatkan getaran ikatan bagi ikatan P-O, rangkaian P-O-P, dan unit PO₂. Tidak ada sebarang petunjuk pada spektrum Raman kaca P_2O_5 -MgO-ZnSO₄ berdop RE (RE = Sm, Dy dan Er) yang mengesahkan penggabungan ion sulfat dalam pembentukan rangkaian. Spektrum penyerapan kaca P_2O_5 -MgO-ZnSO₄ berdop RE (RE = Sm, Dy dan Er) dengan dan tanpa penggabungan zarah nano Ag berasal daripada peralihan elektronik dari aras asas ke pelbagai aras teruja ion RE yang berkonfigurasi elektronik $4f^9$. Spektrum serapan dan pancaran telah digunakan untuk menilai parameter keamatan Judd-Ofelt (JO) dan kebarangkalian peralihan pancaran, nisbah pencabang dan keratan rentas pancaran teransang bagi tiga sistem kaca berdop ion RE (RE = Sm, Dy, dan Er) tersebut. Spektrum PL kaca berdop Samarium pada suhu bilik memperlihatkan empat puncak pancaran berpusat sekitar 562, 599, 644, dan 702 nm, yang terumpu kepada peralihan masing-masing dari $^4G_{5/2}$ ke $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ dan $^6H_{11/2}$. Spektrum PL bagi kaca berdop dysprosium mempamerkan dua puncak yang ketara berpusat sekitar 480 nm dan 574 nm yang masing-masing berpadanan dengan peralihan $^4F_{9/2} \rightarrow ^6H_{15/2}$ dan $^4F_{9/2} \rightarrow ^6H_{13/2}$ dan dua puncak yang rendah. Sebaliknya, sistem kaca berdop erbium telah mempamerkan dua puncak pancaran yang tinggi berpusat pada 541 nm dan 654 nm yang terumpu masing-masing kepada peralihan $^4S_{3/2} \rightarrow ^4I_{15/2}$ dan $^4F_{9/2} \rightarrow ^4I_{15/2}$. Kesemua siri kaca yang mengandungi zarah nano Ag menunjukkan peningkatan keamatan pancaran yang agak banyak, yang terumpu kepada peningkatan kesan medan setempat berperantaraan resonans plasmon permukaan zarah nano di kehampiran ion RE. Sifat keseluruhan setiap siri kaca menunjukkan perubahan yang disebabkan oleh pembedaan zarah nano Ag. Antara semua siri kaca yang terhasil, keratan rentas pancaran teransang untuk peralihan $^4S_{3/2} \rightarrow ^4I_{15/2}$ bagi sistem kaca berdop erbium adalah dianggap sebagai yang tertinggi.

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LIST OF ABBREVIATIONS

BO	Bridging Oxygen
CB	Conduction Band
CR	Cross Relaxation
CW	Continuous Wave
DTP	Dithiophosphate
ET	Energy Transfer
EDFA	Erbium Doped Fiber Amplifiers
ESR	Electron-Spin Resonance
FTIR	Fourier Transform Infrared
GSA	Ground State Absorption
IR	Infrared
JO	Judd-Ofelt
LSPR	Localized Surface Plasmon Resonance
LFE	Local Field Effect
NBO	Non-Bridging Oxygen
NIR	Near Infrared
NMR	Nuclear Magnetic Resonance
NR	Non-Radiative
PL	Photoluminescence
RD	Radiative Decay
RE	Rare Earth
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscope
UV	Ultraviolet
VB	Valence Band
VIS	Visible
XRD	X-Ray Diffraction

LIST OF SYMBOLS

ρ_{ext}	External Charge
2θ	Angle of Diffraction
A	Radiative Probability
A_{ed}	Electric-Dipole Transition Probability
A_{md}	Magnetic-Dipole Transition Probability
B	Magnetic Induction
C	Speed of Light
d	Dielectric Displacement
e	Charge of Electron
E	Electric Field
E_{opt}^{dir}	Direct Optical Band Gap
E_{opt}^{indir}	Indirect Optical Band Gap
F	Field Strength
ΔE	Urbach Energy
f_{cal}	Experimental Oscillator Strength
f_{exp}	Experimental Oscillator Strength
H	Magnetic Field
I	Intensity
J_{ext}	Current Densities
K	Wave vector
m	Mass of Electron
M_{av}	Average Molecular Weight
n	Refractive index
N	Concentration
N_A	Avogadro's number
r_p	Polaron Radius
r_i	Inter Nuclear Distance

R_m	Molar Refraction
S_{ed}, S_{md}	Electric and Magnetic Dipole Line Strengths
T	Temperature
T_c	Crystallization Temperature
T_g	Glass Transition Temperature
T_m	Melting Temperature
t	Time
$\ U^{(i)}\ ^2$	Reduced Matrix Elements
V_M	Molar Volume
W	Weight
α	Absorption Co-efficient
α_m	Molar Polarizability
β	Branching Ratio
ε	Dielectric Function
ε_0	Permittivity of Volume
h	Plank's Constant
ρ	Density of Glass
σ_{emi}	Emission Cross-Section
$\eta(\nu)$	Molar Absorptivity
Ω_i	Judd-Ofelt Intensity Parameters
δ_{rms}	Root Mean Square Deviation between Experimental and Calculated Oscillator Strengths
λ	Wavelength
τ	Lifetime
ν	Wavenumber
$ (S, L)J \rangle$	Electronic State of an Element Defined by its Spin, Orbital and Total Momentums
σ_P^E	Stimulated Emission Cross-Section
$\Delta\lambda_{eff}$	Effective Band Width

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The history of glass may extend back in time to the formation of the earth as mentioned by Porai-Koshits (1990) and Vogel (1994). About thousands of years ago, the first glass prepared by man in furnaces was applied in the ancient art of pottery (Shelby, 2005). The nature of the glass during those old days remained mysterious and unexplored until later. Although some systematic studies on glass composition and their properties along with growth of new glasses occurred, glass preparation with sufficient homogeneity was impossible until 1800 when a new fabrication method was developed by Guinad and Fraunhofer. The glass is capable to be modified both chemical and physical properties of the material by changing the compositions. Compositional modifications which are accompanied by distinct alterations in atomic-level glass structure lead to variations in glass properties. The ability to monitor these atomic-level structure changes as a function of composition may eventually lead to a better understanding of structure/property relationships in glasses.

Besides, due to primitive utility of oxide glasses as decorative pottery to the biocompatible and laser communication technology, they have been and will be used as potential materials in many aspects of ordinary life (Concas *et al.*, 1998; Farok *et al.*, 1994; Wang *et al.*, 1993; Weber, 1990). The most important oxide glasses are silicate glasses (SiO_2), borate glasses (B_2O_3), germanate glasses (GeO_2) and phosphate glasses (P_2O_5). Silicate glasses are of interest with regard to their commercial application structural properties and optical application. Borate glasses are of interest

due to their structures. Rare earth (RE) doped borate glasses have a very high refractive index. Germanium glasses have the important property of transmission of longer wavelength infrared than the silicate glasses but they are limited due to the high cost. Among the three known oxides of phosphates P_2O_3 , P_2O_4 and P_2O_5 ; only P_2O_5 forms glasses. The structure of binary phosphate glasses is based on tetrahedral units. Phosphate glasses can be made with a range of structures from a cross-linked network of Q^3 tetrahedra (vitreous P_2O_5) to polymer-like metaphosphate chains of Q^3 tetrahedra to invert glasses based on small pyro- Q^1 and orthophosphate (Q^0) anions, depending on the $[O]/[P]$ ratio as set by glass composition (Brow, 2000).

The properties of phosphate glasses such as relatively high thermal expansion coefficients, low optical dispersions and low glass transition temperatures compared with their silicate or borate glasses, make them technologically important material in spite of their hygroscopic and poor chemical durability properties (Brow, 2000; Moustafa and El-Egili, 1998). However, most of the existing binary and ternary glass systems contain toxic elements, chemically unstable, highly reactive with water, display powerful devitrification tendency together with complex preparation conditions. During past two decades, continuous efforts have been made to overcome these limitations, where sulfophosphate glasses played a vital role (Da *et al.*, 2011; Da *et al.*, 2010).

Sulphate containing alkali/alkaline phosphate glasses are suitable for electrolytic applications due to their unique electrical properties (Scholz, 2011). The SO_4^{2-} ions largely dissolve in the phosphate glass matrix. There is a weak interaction between SO_4^{2-} ions and metaphosphate ions, resulting in a small dynamic concentration of dithiophosphate (DTP) units. Interaction between these two ions provides suitable environment for incorporation of RE ions to offer high luminescence efficiencies with minimal non-radiative (NR) losses in these glasses. Moreover, the interaction between sulphate and phosphate ions can be modified by the presence of different modifier oxides. Both disruption of the glass network and formation of non-bridging oxygens (NBO) groups are due to the incorporation of alkali-earth oxides in the glass structure (Vogel, 1994). Regard to these facts, structural modifications occur by incorporation of magnesium oxide (MgO) (as modifier) to the zinc sulfophosphate

glasses. REs doped magnesium-zinc-sulfophosphate glasses are technologically prospective due to their several unique attributes. The RE doped glasses have gained some attention due to high dielectric constants, a wide band infrared transmittance and large third order non-linear optical susceptibility (Auzel *et al.*, 2001; Chilloce *et al.*, 2006; Inoue *et al.*, 2002b; Jha *et al.*, 2000; Kumar *et al.*, 2003; Mori *et al.*, 1997; Prakash *et al.*, 2001; Souza *et al.*, 2002; Tanabe *et al.*, 2002).

Amongst various RE ions, samarium (Sm^{3+}) reveals most remarkable luminescence properties (Brahmachary *et al.*, 2015; Carnall *et al.*, 1968; Lin *et al.*, 2007; Venkatramu *et al.*, 2007). Sm^{3+} ion is well-suited to explore the energy transfer processes because of its lowest emitting level $^4\text{G}_{5/2}$ possesses relatively higher quantum efficiency and shows different quenching channels. Sm^{3+} ions are added to glass to create prominent orange-red color or unique optical properties to make lasers for special applications (Elisa *et al.*, 2013; Lim *et al.*, 2013; Thomas *et al.*, 2013). In its usual oxidized form, it is added to ceramics and glasses to increase the absorption of infrared light. Sm^{3+} ions are also combined with many other substances under relatively mild conditions. Looking at these wealthy prospects, sulfophosphate system with Sm^{3+} are prepared in order to achieve lasing glass material. In addition, Sm^{3+} ions are exploited for high-density optical storage, under sea communication and color displays.

Another lanthanide ion chosen for the present study is dysprosium (Dy^{3+}) ion. Since the $^6\text{F}_{11/2} (^6\text{H}_{9/2}) \rightarrow ^6\text{H}_{15/2}$ transition of Dy^{3+} around 1.3 μm is found to be useful for the optical amplification and its visible upconversion emission can be used as a solid state laser, this RE ion received much practical attention (Heo and Shin, 1996; Kityk *et al.*, 2002; Yang *et al.*, 2005). Dy^{3+} gives very strong emission in yellow region, which is expected to give lasing from $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{7/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{9/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ consider as emission transitions for Dy^{3+} ions in the visible and near infrared (NIR) regions. Among these emission transitions, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (electric dipole) in yellow and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (magnetic dipole) in blue regions are the main transitions (Babu and Jayasankar, 2000).

Erbium (Er^{3+}) as a RE ion has played an important role in the development of broadband erbium-doped fiber amplifiers (EDFA) (Auzel *et al.*, 2001; Jha *et al.*, 2000; Kumar *et al.*, 2003; Prakash *et al.*, 2001; Tanabe *et al.*, 2002). Optical properties of Er^{3+} ion in various glasses make it as a promising materials for the optical application for instance, it can be used as a solid-state laser due to its 1.54 μm emission and it can be used as a solid-state laser because of its visible upconversion emission.

RE doped glasses are applicable in various practical application such as optical amplifiers, optical recording, infrared sensors, laser active media and infrared-to-visible converters (Xiao and Yang, 2007). Earlier, the good characteristics of RE doped glasses such as nonlinear optical performance and optical bi-stability have been reported. Besides, high RE ions solubility, good thermal and mechanical stability, low cutoff phonon energy, higher refractive indices than the silicates and fluoride glasses, large amplification bandwidth and enhanced luminescence are the remarkable characteristics of RE doped glasses (Liu *et al.*, 2007; Sahar *et al.*, 2008). As the results of these notable advantages, they become promising candidates for photonic applications such as window materials and optical memory (Xiao and Yang, 2007). In order to make devices with optimized photonic properties, usually, the RE ion concentration needs to be kept low to minimize luminescence quenching (Jlassi *et al.*, 2010; Shen *et al.*, 2007). Since the absorption cross-section of majority of RE ions in such glasses are very small, some modifications are needed to improve it for applications (Lin *et al.*, 2004). One way is to exploit energy transfer from a RE with a large absorption cross-section to the RE with small absorption cross-section (Lin *et al.*, 2003b; Lin *et al.*, 2004; Madden and Vu, 2009; Mirgorodsky *et al.*, 2006; Rai and Rai, 2007). RE ion environment by embedding metallic nanoparticles can be modified to compensate the harmful effect of quenching (Amjad *et al.*, 2013; Eroni *et al.*, 2009; Kassab *et al.*, 2008; Kassab *et al.*, 2009; Li *et al.*, 2004; Lin *et al.*, 2008; Rai and Rai, 2007; Singh *et al.*, 2010; Ueda *et al.*, 2009).

Glasses embedded with metallic nanoparticles have received much attention because of their notable optical properties that could lead to the development of new solid-state short-wavelength lasers, biological labelling and efficient solar cells (Švrček *et al.*, 2004). The luminescence intensity RE doped glasses can be enhanced

by embedding the semiconducting and metallic nanoparticles. The excitation or luminescence wavelength is near to the surface plasmon resonance (SPR) wavelength for metallic nanoparticles and must be greater than optical band gap energy for semiconducting nanoparticles. The preparation and characterization of RE doped glasses embedded with metallic nanoparticles have been studied by many researchers in the past few years (Almeida *et al.*, 2008; Carmo *et al.*, 2009; Jimé'nez *et al.*, 2010). Several attempts have been made to indicate that luminescence efficiency of the glass matrix containing RE ions can be enhanced by the presence of nanoparticles inside it (Carmo *et al.*, 2009; de Almeida *et al.*, 2008; Manoj Kumar *et al.*, 2003; Mattarelli *et al.*, 2007). In all these studies, the large local field on the RE ions present within the vicinity of metallic nanoparticles and the energy transfer from metallic nanoparticles to the RE ions are responsible for luminescence enhancement. In the previous reported studies, various nanoparticles such as Au, Ag, AgCl, CuCl, CdSe, CdTe have been introduced into glasses to improve the optical nonlinearity to a big extent (Amjad *et al.*, 2013; Kassab *et al.*, 2009; Lin *et al.*, 2003b; Lin *et al.*, 2008; Mirgorodsky *et al.*, 2006).

Size-controlled optical properties of silver (Ag) nanoparticles are promising material for technological applications such as diffraction elements, optical filters, nanoplasmonic devices, bi-sensors, and nonlinear media (Nikonorov *et al.*, 2010). Ag nanoparticles can be made in various media such as water solutions, polymers, glasses, and crystalline media. In addition, the inorganic glasses are the unique matrix for Ag nanoparticles formation. Ag nanoparticles size within the wide range can be controlled by means of altering the temperature and duration of thermal processing in the inorganic glasses due to the wide temperature range of glass viscosity growth in these glasses (Nikonorov *et al.*, 2010). In regard to this fact, controlling and exploring all the stages of Ag nanoparticles formation including the starting stage is possible in this kind of matrix (Nikonorov *et al.*, 2010).

Few studies have been made on metallic nanoparticles embedded RE doped phosphate glasses. Silicate or tellurite are the usual host matrix that phenomenon of enhanced luminescence have been investigated. Phosphate glasses are widely applicable in photonic applications as a consequence of their mechanical properties

and ability to accept higher concentration of RE ions, however, they have not received much attention in the field of plasmonics or nanophotonics. Specifically, there is no report on metallic nanoparticles embedded inside the magnesium-zinc-sulfophosphate glass matrix with RE ions. Regards to this matter, deeper study of the effect of nanoparticles on luminescence enhancement and energy transfer processes in the magnesium-zinc-sulfophosphate glass matrix is necessary.

1.2 Problem Statement

Since phosphate glasses also have a very high solubility for RE ions, many researchers have been reported the properties of phosphate glasses doped with RE ions. For example, the photoluminescence properties of the Dy³⁺-doped and Dy³⁺-Tm³⁺ co-doped phosphate glasses have been studied by absorption, excitation and emission spectra (Liang *et al.*, 2008). The observation of white light is allowed when the glasses are excited by the ultraviolet light because a combination of blue and yellow emissions has emerged in the glasses. Spectral properties of Nd³⁺ and Dy³⁺ ions in different phosphate glasses have been studied by Seshadri *et al.* (2010) and several spectroscopic parameters such as Judd-Ofelt intensity parameters, radiative transition probabilities and radiative lifetimes of certain excited states of these RE ions in these glass matrices have been reported. Other researchers (Kesavulu and Jayasankar, 2012; Lim *et al.*, 2013; Rao *et al.*, 2011; Reddy *et al.*, 2011; Sreedhar *et al.*, 2013) investigated the effects of RE ions on luminescence properties of the glasses. Although a large number of studies has been done on luminescence and structural properties of RE doped phosphate glasses, the luminescence and structural features of RE³⁺ (RE = Sm, Dy and Er) doped magnesium-zinc-sulfophosphate glasses are rarely investigated.

Moreover, emission characteristics of RE ions are enhanced by the presence of the metal. The preparation and characterization of RE doped glasses embedded with metallic nanoparticles have been studied by many researchers in the past few years (Carmo *et al.*, 2009; de Almeida *et al.*, 2008). For instance, Naranjo *et al.* (2005) reported down conversion luminescence enhancement for Pr³⁺-doped lead-germanate

glass containing silver nanoparticles. But, the influence of embedded silver nanoparticles on optical and structural features of RE^{3+} ($RE = Sm, Dy$ and Er) doped magnesium-zinc-sulfophosphate glasses has not been studied yet.

1.3 Research Objectives

In line with the aim of the research, the followings are the research objectives:

- i. To determine the structural and physical features of RE^{3+} ($RE = Sm, Dy$ and Er) doped magnesium-zinc-sulfophosphate glass with and without incorporation of Ag nanoparticles
- ii. To determine the influence of RE^{3+} ($RE = Sm, Dy$ and Er) concentration on the optical properties of magnesium-zinc-sulfophosphate glass with and without Ag inclusion
- iii. To analyse the Judd-Ofelt analysis for magnesium-zinc-sulfophosphate in the presence of various concentration of RE^{3+} ($RE = Sm, Dy$ and Er) and Ag nanoparticles

1.4 Significance of Research

The importance of the study is to obtain high efficiency of luminescence in glasses. The significant of research are as follows:

- i. To demonstrate the influence of the RE^{3+} ($RE = Sm, Dy$ and Er) on the structural and optical properties of magnesium-zinc-sulfophosphate glasses. Therefore, the outcomes of the study contribute better understanding towards the behaviour of the RE^{3+} ($RE = Sm, Dy$ and Er) on the luminescence enhancement since these glasses are applicable in many optical devices due to their potential applications.

- ii. To study the effects of the Ag nanoparticles on the optical properties of RE^{3+} ($RE = Sm, Dy$ and Er) doped magnesium-zinc-sulfophosphate glasses. Consequently, it provides promising materials with enhanced optical properties for photonic devices, such as, sensors, solid state lasers, and optical switches.

1.5 Scope of the Study

In this study, RE^{3+} ($RE = Sm, Dy$ and Er) doped and undoped magnesium-zinc-sulfophosphate glass as well as RE doped magnesium-zinc-sulfophosphate glass containing Ag nanoparticles were prepared. Investigation of structural and optical properties were the main purposes of the study. The structural properties can be determined by X-Ray diffraction (XRD) spectroscopy, Fourier Transformed Infrared (FTIR), and Raman spectroscopy. Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) and photoluminescence (PL) spectroscopy were operated to describe the optical properties. In order to observe the small structure of nanoparticles embedded in samples, the Transmission Electron Microscope (TEM) was utilized.

1.6 Outline of Thesis

This thesis is composed of six chapters and three appendices. The summaries of the chapters are as follows:

Chapter 1 presents the background of the study, statement of the problems, research objectives, scope of the study and brief review on characterization tools.

Chapter 2 explains briefly about Judd-Ofelt theory. Furthermore, literature are invoked to describe the sulfophosphate glass.

Chapter 3 explains the experimental procedure to synthesize the studied sample glass. In addition, instruments and their fundamental concepts which have been operated to characterize the sample glass are also introduced.

Chapter 4 describes the effect of RE^{3+} ($RE = Sm, Dy$ and Er) ions on structural and optical properties of magnesium-zinc-sulfophosphate glass.

Chapter 5 presents general descriptions of the influence of the nanoparticles on structural and optical properties of RE^{3+} ($RE = Sm, Dy$ and Er) doped magnesium-zinc-sulfophosphate glass. In this chapter, new RE^{3+} ($RE = Sm, Dy$ and Er) doped glasses containing metallic Ag nanoparticles were prepared using melt quenching technique. They were characterized to investigate the structural and optical properties.

Chapter 6 gives the conclusion of the research and some recommendations for future works.

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