

STRUCTURAL, OPTICAL AND JUDD-OFELT PARAMETERS STUDY ON
SAMARIUM AND DYSPROSIUM IONS DOPED CALCIUM SULFATE AND
MAGNESIUM SULFATE ULTRA-PHOSPHATE GLASSES

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DEDICATION

This thesis is dedicated to my father (Malan Mohammed C. Aliyu), who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother (Hajiya Habiba Mohammed Aliyu), who taught me that even the largest task can be accomplished if it is done one step at a time.

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ABSTRACT

Trivalent rare earth (Dy^{3+} and Sm^{3+}) doped calcium sulfophosphate, $20\text{CaSO}_4-(80-x)\text{P}_2\text{O}_5-x\text{Dy}_2\text{O}_3$, $20\text{CaSO}_4-(80-x)\text{P}_2\text{O}_5-x\text{Sm}_2\text{O}_3$ and magnesium sulfophosphate $20\text{MgSO}_4-(80-x)\text{P}_2\text{O}_5-x\text{Dy}_2\text{O}_3$, $20\text{MgSO}_4-(80-x)\text{P}_2\text{O}_5-x\text{Sm}_2\text{O}_3$ with $0.2 \leq x \leq 1.5$ mol% of ultra-phosphate glass system were prepared using conventional melt-quenching method followed by annealing process at 300 °C for 4 hours. The amorphous phase of glass samples were characterized by X-ray diffraction (XRD) method, while the structural features of the samples were measured using Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The optical properties of glass samples were characterized by ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy and photoluminescence (PL) spectroscopy. The infrared spectra revealed the bonding link of the host affected by modifier oxides (MgO, CaO) and intermediate oxides (SO_4). Their linkages consist of P-O-P network, PO_2 units, PO-, P=O, O-S-O and SO_4 groups with no evidence of rare earth ions network as a result of the low concentrations of dopant. In addition, the similar tetrahedral arrangement was also shown by Raman spectra. The NMR spectra were used to identify the phosphate compositional change through conversion of Q^3 (in P_2O_5) to Q^2 , Q^1 and Q^0 which follow the predictions of the Van Wazer's model. The NMR spectra affirmed the presence of Q^3 , Q^2 , and Q^1 groups, referring to existence of ultra-, meta- and pyrophosphate units, although the Q^2 and Q^1 are more predominant. Changes in Q^n distributions in host phosphate networks are due to the breaking of P-O-P linkages to form P-O-M networks (where M is metal ions). The physical and nuclear properties such as density, molar volume, field strength, oxygen packing density, ionic packing density, inter nuclear distance, ion concentration and polaron radius were evaluated. The absorption characteristic presented by the UV-Vis-NIR spectra showed eight peaks from transition of Sm^{3+} , and six peaks for transition of Dy^{3+} ions. All transitions correspond to the transition from ground state to excited state of Sm^{3+} and Dy^{3+} ions, respectively. The energy gap ranges from 4.090 – 4.185 eV, 4.517 – 4.612 eV and Urbach energy from 0.105 – 0.119, 0.155 – 0.135 eV with respect to the rare earth ions content. The photoluminescence spectra of Dy^{3+} ions illustrate three prominent bands around 481 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$), 577 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$), and 660 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$), and for Sm^{3+} ions five peaks were observed around 560 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$), 597 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$), 642 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$), 703 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$) and 735 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{13/2}$). The absorption and emission spectra were used to evaluate the Judd-Ofelt parameters and radiative properties such as transition probabilities, radiative lifetimes and branching ratios of rare earth ions. Based on this study, calcium sulfophosphate glass and magnesium sulfophosphate glass doped with rare earth ions could be suggested as promising luminescent host material for solid-state lighting device application.

ABSTRAK

Nadir bumi tiga valensi (Dy^{3+} dan Sm^{3+}) dop kalsium sulfofosfat $20\text{CaSO}_4-(80-x)\text{P}_2\text{O}_5-x\text{Dy}_2\text{O}_3$, $20\text{CaSO}_4-(80-x)\text{P}_2\text{O}_5-x\text{Sm}_2\text{O}_3$ dan magnesium sulfofosfat $20\text{MgSO}_4-(80-x)\text{P}_2\text{O}_5-x\text{Dy}_2\text{O}_3$, $20\text{MgSO}_4-(80-x)\text{P}_2\text{O}_5-x\text{Sm}_2\text{O}_3$ dengan $0.2 \leq x \leq 1.5$ mol% dalam sistem kaca ultra-fosfat telah disediakan dengan menggunakan kaedah pelindapan lebur lazim yang diikuti dengan proses penyepuhlingapan pada 300°C selama 4 jam. Fasa amorfus sampel kaca telah dicirikan oleh kaedah pembelauan sinar-X (XRD), sementara ciri-ciri struktur sampel telah diukur menggunakan spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi Raman dan spektroskopi resonans magnet nuklear (NMR). Sifat optik sampel kaca dicirikan melalui spektroskopi ultraungu-cahaya nampak inframerah dekat (UV-Vis-NIR) dan spektroskopi fotoluminesens. Spektrum inframerah menunjukkan hubungan ikatan hos terjejas oleh oksida pengubahsuai (MgO, CaO) dan oksida pertengahan (SO_4). Hubungan rangkaian terdiri daripada P-O-P, unit PO_2 , PO-, P=O, O-S-O dan kumpulan SO_4 , tanpa menunjukkan rangkaian ion-ion nadir bumi disebabkan oleh komposisi dopan yang rendah. Tambahan pula, susunan tetrahedral yang sama juga ditunjukkan oleh spektrum Raman. Spektrum NMR telah digunakan untuk mengenal pasti perubahan komposisi fosfat melalui penukaran Q^3 (dalam P_2O_5) kepada Q^2 , Q^1 dan Q^0 yang mengikuti ramalan model Van Wazer. Spektrum NMR menegaskan kehadiran kumpulan Q^3 , Q^2 , dan Q^1 yang merujuk kepada kehadiran unit ultra-, meta- dan pirofosfat walaupun Q^2 dan Q^1 lebih dominan. Perubahan dalam taburan Q^n dalam rangkaian hos fosfat adalah disebabkan oleh pecahnya rangkaian P-O-P untuk membentuk rangkaian P-O-M (M merupakan ion logam). Ciri-ciri fizikal dan nuklear seperti ketumpatan, isipadu molar, kekuatan medan, ketumpatan kepadatan oksigen, ketumpatan padatan ionik, jarak antara nukleus, kepekatan ion dan jejari polaron telah ditentukan. Ciri penyerapan yang ditunjukkan oleh spektra UV-Vis-NIR menunjukkan lapan puncak dari peralihan ion Sm^{3+} dan enam puncak untuk peralihan ion Dy^{3+} . Semua peralihan adalah masing-masing sepadan dengan peralihan dari keadaan asas ke keadaan teruja ion Sm^{3+} dan Dy^{3+} . Jurang tenaga berjulat dari 4.090 – 4.185 eV, 4.517 – 4.612 eV dan tenaga Urbach dari 0.105 – 0.119 eV, 0.155 – 0.135 eV menurut kandungan ion nadir bumi. Spektrum fotoluminesens bagi ion Dy^{3+} menunjukkan tiga jalur yang menonjol sekitar 481 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$), 577 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$), and 660 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$), dan bagi ion Sm^{3+} lima puncak telah dicerap sekitar 560 nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$), 597 nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$), 642 nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$), 703 nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{11/2}$) and 735 nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{13/2}$). Spektrum serapan dan pancaran telah digunakan untuk menentukan parameter Judd-Ofelt dan sifat pancaran seperti kebarangkalian peralihan, masa hayat pancaran dan nisbah cabang ion nadir bumi. Berdasarkan kajian ini, kaca kalsium sulfofosfat dan kaca magnesium sulfofosfat yang didop dengan ion nadir bumi boleh dicadangkan sebagai bahan hos luminesens berpotensi bagi aplikasi peranti pencahayaan keadaan pepejal.

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LIST OF ABBREVIATIONS

ASTM	-	American society for testing materials
A	-	Absorbance
BO	-	Bridging Oxygen
CSA	-	Chemical shift anisotropy
CRN	-	Continuous random network
CF	-	Crystal field
DFT	-	Density function theory
DTA	-	Differential thermal analysis
EDX	-	Energy dispersive X-ray spectroscopy
E	-	Electric field
ED	-	Electric dipole
EM	-	Electromagnetic field
FTIR	-	Fourier Transform Infrared
IR	-	Infrared
HF	-	Hydrogen fluoride
JO	-	Judd-Ofelt
KBr	-	Potassium bromide
LED	-	Light emitting diode
LNS	-	Local network structure
LRO	-	Long range order
MAS	-	Magic angle spinning
MD	-	Magnetic dipole
MRN	-	Modified random network
NBO	-	Non bridging oxygen
NIR	-	Near infrared region
NMR	-	Nuclear magnetic resonance
NPs	-	Nano-particles
NR	-	Non radiative
O/P	-	Oxygen to phosphate ratio
OPD	-	Oxygen parking density

PGs	-	Phosphate glass structure
PL	-	Photoluminescence
OPO	-	Oxygen-phosphorus-oxygen
P=O	-	Terminal oxygen
P:S	-	Phosphate to sulfur ratio
RF	-	Radio frequency
RMS	-	Root mean square
REIs	-	Rare earth ions
SEM	-	Scanning electron microscope
SQF	-	Spectroscopic quality factor
SRO	-	Short range order
TGA	-	Thermo-gravimetric analysis
UV	-	Ultraviolet
Vis	-	Visible
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

A_{rad}	-	Radiative transition probability
A_{ed}	-	Electric-dipole transition
A_{md}	-	Magnetic-dipole transition
$A_{\text{T(total)}}$	-	Total radiative transition probability
B_0	-	Magnetic field
β_r	-	Branching ratio
β	-	Nephelauxetic ratio
c	-	Speed of light
e	-	Electric charge
E_{op}	-	Optical absorption
E_{opt}	-	Optical band gap
ϵ	-	Dielectric constant
$\epsilon(\nu)$	-	Molar extinction coefficient
ϵ	-	Torsional vibration
f_{exp}	-	Experimental oscillator strength
f_{cal}	-	Calculated oscillator strength
h	-	Plank's Constant
I_{int}	-	Initial intensity
I_{tran}	-	Transmitted intensity
ρ	-	Density
n	-	Refractive index
m	-	Mass
μ	-	Reduced mass
λ	-	Lambda
ν	-	Wave number
ν_{as}	-	Asymmetric vibration
ν_{ss}	-	Symmetric vibration
γ	-	Gyromagnetic ratio
θ	-	Brag's angle
τ_{rad}	-	Lifetime

Q^3	-	Ultra-phosphate
Q^2	-	Meta-phosphate
Q^1	-	Poly/Pyrophosphate
Q^0	-	Ortho-phosphate
α_{ep}	-	Thermal expansion
δ_{cha}	-	Chemical shift anisotroph
δ	-	Bending vibration/Bonding parameter
ω	-	Angular frequency
R_m	-	Molar refractivity
α_{ep}	-	Molar polarizability
α_e	-	Electronic polarizability
M	-	Metallization Criterion
N_A	-	Avogadro's constant
ϵ_{opt}	-	Optical dielectric constant
T_c	-	Crystallization temperature
T_g	-	Glass transition temperature
T_m	-	Melting temperature
$\ U_\lambda\ $	-	Reduced matrix

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Glass is an amorphous solid material which displays the structural characteristics of liquid having a glass transition (T_g). It is typically brittle, some are transparent and plays a vital role in the progress of society, and used for decoration as window panes, packaging (Jars for food, bottles, for drinks), housing and building, fibre optic cables etc. According to the American Society for Testing Materials (ASTM) defined glass as "an inorganic product of fusion, which has been cooled to a rigid condition without crystallizing". It is a mixture of sand and other minerals melted together at very high temperature (normally between 900 and 2000°C). The exact melting temperature depends on the glass composition. Chemically, a glass is actually like a liquid at room temperature, it became softer gradually at higher temperature and more like a liquid which allows the glass to be poured, blown, pressed and mould into different shapes. Even though, there are other methods used in glass formation, it can be formed by chemical vapour deposition (CVD), by sol-gel processing of solution, thermal evaporation techniques (TET), Sputtering techniques and by neutron irradiation of crystalline materials (Shelby and Schubert, 1997).

The oxides glasses are formed when metals combine with oxygen, the principles that classified cations in glass network are categorized in 3 stages these are; Glass formers, Modifiers and Intermediate glasses.

Network modifiers are alkali or alkaline earth metals oxides that break or interrupt the network when they are added to the host materials to increase the workability of a glass, examples are CaO, MgO and Na₂O₃ etc.

Intermediate are oxides capable of entering the network of glass formers, sometimes to re-enforce other networks. They act as network formers like aluminum, but ordinarily, they cannot form glass network themselves rather they join existing glass networks added to obtain a special properties examples: Al_2O_3 , Ti_3O , TeO_2 , SeO_2 , WO_3 etc (Hussin, 2011) including SO_4 .

Addition of modifier oxides e.g K_2O ; Rb_2O to basic constituent (network former) such as Phosphate, borate, silicate etc can alter the structure and physical properties depending on the quantity added, the properties of modified glass show a non-linear behaviour with a gradual increase in alkali oxide. The deviation from linearity causes the host anomaly (Saddeek, 2004). The structure of binary phosphate is similar to that of binary silicate based on the tetrahedral structure. This structure depends on the phosphate content and the content of glass modifier oxides, such as CaO , MgO , and Na_2O etc. Addition of glass modifier to phosphate glass will increase its durability and results in the cleavage of P-O-P linkages to form non-bridging oxygen's (NBOs) thereby disrupting the structure of the glass having covalent P-O-M bonds and also ionic cross-linkages between non-bridging oxygen (NBOs).

The glass formers are the major bulk materials that result in the formation of glasses viz: Tellurium oxide (TeO_2), Silicon dioxide (SiO_2), Phosphorus pentoxide (P_2O_5) and Boron trioxide (B_2O_3) etc. Other constituent of glasses are the flux responsible for reducing the melting temperature of the glass former such as PbO , even though, certain times may lead to the changes in properties of the glass former, while colour additive are added to give out a colour to the glass e.g. silver or gold. The Fining/Refining agents are to improve the quality characteristics of the glass by removing bubbles examples, arsenic, antimony oxides etc.

Phosphate glasses differ from other glass-former due to the existence of terminal oxygen on each network, results in less cross-link, such as terminal oxygen (TO) limit the connectivity of phosphate glass structure (PGs) and reduces their inter-atomic forces and rigidity. This may cause easy in the de-polymerisation process. Furthermore, phosphate-based glasses contain a lesser cross-link with the high number of TO atoms. When mixed with other metal oxides result in higher flexibility of p_4^{3-}

tetrahedra. For this reason, ranges of phosphate glass formation are expected to be wider than the other based glasses (Egan *et al.*, 2000). It has the ability to dissolve completely in an aqueous solution, and the dissolution rate is sensitive to glass composition (Bunker *et al.*, 1984). This indicates that phosphate-based glasses have numerous advantages over the other based glasses due to superior physical properties e.g high ultraviolet (UV) transmission (Brow, 2000), high electrical conductivity (Shih *et al.*, 2003). This is suitable candidates for technological applications as optical fibers for data transmission, host glasses for solid state lasers, solid state batteries and glass-to-metal sealing (Hassan and Hafid, 2004), poor chemical durability can often limit their suitability, although can be improved by modifier addition. It also has high thermal expansion coefficients (258×10^{-7} to $99 \times 10^{-7}/^{\circ}\text{C}$) low melting temperature and low glass transition temperature (T_g below 420°C) depending on composition (Shih *et al.*, 1998). Low softening temperatures of phosphate glasses make it suitable for hermetic seals (Marzouk *et al.*, 2017).

However, the thermal expansion (α_{ep}) of the glass depends on the asymmetry of the amplitude of thermal vibrations in the glass. Therefore, the thermal vibration is small when there are many strong bonds present in the network. These properties make them useful candidates for fast ion conducting materials and other important applications (Hassan and Hafid, 2004).

Ultra-phosphate glass region, are categories of phosphate glass with $\text{RO}/\text{P}_2\text{O}_5$ ratio less than one, where RO or R_2O is the modifying oxides, despite the fact that hydroxyl (OH) group may serve as a modifier which affects the optical and thermal properties of the glass but often neglected. Ultra-phosphate region mostly has a longer terminal oxygen (P=O) and a shorter P-O Q^3 bond length when compared with any of the phosphate polymorphs (Mercier *et al.*, 1999). It is easier in de-polymerization processes.

Sulphur species are found in oxide glasses and melts of volcanic process. Commercially, silica glasses batches contain low levels of sulphur (< 0.2 wt.% S) which are deliberately added in the form of sulphate refining agent or as sulphide to provide a uniquely amber colour (Bingham and Hand, 2008), sulfur when mixed with

phosphate glasses are satisfied in immobilizing radioactive waste. Many glasses materials are thermally and chemically stable having good electrical conductivity and compatibility with electrode materials with a small amount of sulphur. Cadmium sulphides attract more interest in the field of integrated optics, opto-electronics and photovoltaic devices with a higher quantity of sulfur. The studies are consistent with the hypothesis, that sulphur interact with phosphate network by occupying the interstice spaces of oxygen in non-bridging position as a weaker cation-network interaction, the results in an increased in conductivity within mol % of Sulphur (Chowdari *et al.*, 1993).

Many types of radioactive waste were certainly incorporated in glass for long-term safe storage (i.e vitrified) contains a larger amount of sulphur. Generally, low solubility of sulphate in silicate (SiO_2) melts. In oxidation conditions where a waste glass melt could be safely operated and this can result in sulphur becoming the waste-loading limiting constituent (McKeown *et al.*, 2001). Meanwhile, much is still required to know more about the relationship between sulfur solubility in phosphate glass system.

Rare earth ions (REI) comprises of lanthanide and actinide, the lanthanides are known elements in $4f$ shell level located insides the atom. Their spectra arising from $4f-4f$ transitions which are narrow and insensitive to their environment, unlike transition metal in $3d$ spectra, transitions of these elements by excitation and de-excitation causes emissions which are detected in the infrared, visible, or ultraviolet region. These ions -doped glasses have attracted more attention due to their usefulness in many optical applications such as optical fibers and solid state lasers (Amjad *et al.*, 2013). For optical amplifier applications as well as lasers, host glasses such as phosphate, boro-tellurite, and fluoro-iodate glasses are the vastly promising candidate (Florez *et al.*, 2000). The ions incorporated in glasses are extensively used in order to activate the luminescence and optical materials. The studies provide fundamental data on radiative properties such as transition probability, radiative life-time, branching ratios and are used for optical device.

Trivalent RE ions -doped phosphate glasses have been developed basically for IR active optical devices (Sava *et al.*, 2013). The ions attract higher demand for various visible lasers and many other light sources when doped with host glasses. Further research was developed on phosphate based glasses doped Dy^{3+} Tb^{3+} Er^{3+} and Eu^{3+} (Pisarska *et al.*, 2011) which identify the various colors of red, orange, blue, yellow and violet/blue emission. However, this work differs with Pisarka by modifier oxides and the dopant.

The calcium/magnesium sulfate ultra-phosphate glasses –doped rare earth (Sm^{3+} and Dy^{3+}) has been chosen to improve the quality of glasses. The research aims to investigate the structure and optical properties of calcium/magnesium sulfate ultra-phosphate glasses, this may help to verify the luminescence properties of RE materials for better efficiency, hoping that the quantitative estimate on both the structure and optical studies would be accurate.

1.2 Research Problem

Phosphate glass was recognized as a valuable material in optical glasses. Incomparable features of phosphate in the structure or optical stability attract more attention to many researchers, but due the hygroscopic and volatility in phosphate reduces its performance in many applications, this can also have limitations in their low absorption and emission cross-section. Other anomalous behaviours in phosphate glasses contribute to its setback in vitreous phosphate pentoxide (P_2O_5). Ultra-phosphate on the other hand, is chemically unstable with regards to hydrolysis of P-O-P bonding by atmospheric moisture attack which mean the vitreous phosphate have low resistance to moisture (Lu *et al.*, 2015) and the same time.

Ultra-phosphate region has every tendency in becoming crystal. Hence, if the chemical durability were identified the potential application needs to be expanded accordingly. To improve the required performance by choosing a suitable modifier oxide such as CaO, MgO, ZnO, PbO etc, magnesium oxide added to phosphate exhibit a higher forming ability (Karakassides *et al.*, 2004). Many researchers are more

interested to study the structure and luminescence properties of binary or multi-component phosphate glasses doped with RE ions. Studies on the structural features of the phosphate-based glass system especially in the composition of calcium sulfo-phosphate and magnesium sulfo-phosphate glasses need to be the focus. The effects of doping RE ions (Sm^{3+} and Dy^{3+}) on its optical and luminescence properties and the influence of the ions on the structural features need to be studied. The calculated values of Judd-Ofelt parameters will be utilized in evaluating the various radiative parameters such as transition probabilities radiative lifetimes and branching of rare earth ion (REI).

1.3 Research Objectives

The objectives of the research are:

- (a) To determine the amorphous phase of un-doped $x\text{CaSO}_4 (80-x) \text{P}_2\text{O}_5$, $x\text{MgSO}_4 (80-x) \text{P}_2\text{O}_5$ and doped $20\text{CaSO}_4 (80-x) \text{P}_2\text{O}_5-x\text{Sm}_2\text{O}_3$, $20\text{MgSO}_4 (80-x) \text{P}_2\text{O}_5-x\text{Dy}_2\text{O}_3$ at different concentration.
- (b) To determine the influence of calcium sulfate/ magnesium sulfate as a modifier oxide on the structure and physical properties of ultra-phosphate based glasses.
- (c) To determine the effect of rare earth ions (Sm^{3+} and Dy^{3+}) on optical (e.g Band gap, Urbach energy) and luminescence properties of calcium sulfate/ magnesium sulfate ultra-phosphate glasses at different concentration.
- (d) To evaluate the Judd-Ofelt intensity parameters (Ω_λ) from experimental and calculated oscillator strength for Sm^{3+} and Dy^{3+} ions so as to demonstrate the validity of the theory and to verify the optical quality of the materials..

1.4 Scope of the Research

In achieving the objectives, the work has the following scope.

- (a) The amorphous phase of the samples was determined by X-ray diffraction (XRD) spectroscopy for calcium sulphate/magnesium sulfate ultra-phosphate glass doped dysprosium and samarium ion prepared by the melt-quenching method.
- (b) The structural characterization was also investigated using FTIR, Raman and NMR spectroscopy,
- (c) Optical and luminescence characterization were identified using Photoluminescence and UV-Vis-NIR spectrometer.
- (d) Judd-Ofelt intensity parameter was analyzed and compared with those in literature

1.5 Significant of Research

The spectroscopic study of phosphate glass doped and un-doped rare earth (RE) helped in developing material for optical data transmission, laser amplification, fibre optical amplifier or biomedical applications. Phosphates were chosen as a host due to its low transition temperature and are well fitted for doping RE ions for optical devices (Marino *et al.*, 2001). Phosphate encourages de-polymerization process owing to terminal oxygen availability, de-polymerization is important in increasing the phosphate durability. Also, the used of ultra-phosphate (Q^3) glasses phase contain a relatively larger amount of hydroxyl group responsible for protonic conductor (Mercier *et al.*, 1998, Mercier *et al.*, 1999), another side, lesser work has been observed on ultra-phosphate glass phase.

Due to the limited research based on $x\text{CaSO}_4-(100-x)\text{P}_2\text{O}_5$ and $x\text{MgSO}_4-(100-x)\text{P}_2\text{O}_5$ glass system doped rare earth ions. Therefore, the present study is aimed to

understand the effect of RE³⁺ (Sm³⁺, Dy³⁺) ions and to analyze the optical and luminescence properties of the samples. Consequently, the spectroscopic studies will give information about the efficiency of the samples; it can also give a better understanding of the structural and optical features of sulphate containing alkaline earth. The remarkable outcomes of this study will help in developing many functional glasses and long afterglow material. Therefore, knowing the structure and optical and luminescence characteristics of the glass system will contribute to the new knowledge in material field.

1.6 Thesis Plan

Preparation and characterization of REI (Sm³⁺ and Dy³⁺) doped phosphate-based glasses using conventional melt quench method will be discussed below, the thesis comprises of five chapters viz;

Chapter 1: Present the background of the research and an overview mentioned with emphasis on the development of phosphate glasses including the behaviour of REI, research problems, research objectives, scope of research and significance of the study including the thesis outline.

Chapter 2: Explores the literature review on magnesium/calcium sulfo-phosphate glasses with other modifier oxides; Phosphate based glass, modifier pseudoreaction on phosphate glass, XRD, FTIR, Raman and NMR analysis on phosphate glass, Structure by IR, Raman and NMR, optical, luminescence properties and the Judd-Ofelt analysis was also discussed.

Chapter 3: Demonstrate the experimental method which includes Samples preparation by the melt-quench method, samples instrumentation on XRD, FTIR, Raman, NMR, UV-Vis-NIR and Photoluminescence spectroscopy.

Chapter 4: The results of our findings were discussed in this chapter which serves as the most important part of the thesis.

Chapter 5: Conclusion and the future perspectives

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