

STRUCTURAL, LUMINESCENCE PROPERTIES AND JUDD-OFELT
ANALYSIS OF RARE-EARTH DOPED CALCIUM-SULFOBOROPHOSPHATE
AND BARIUM-SULFOBOROPHOSPHATE GLASSES

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DEDICATION

This thesis is dedicated to my beloved

Father, Alhaji Abdullahi Yamusa, Mother, Hafsat Abdullahi, Wife, Rahma Sani Yamusa, Children, Aisha Yamusa Abdullahi and Hafsat Yamusa Abdullahi for their support and encouragement.

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ABSTRACT

Glass samples of undoped calcium-sulfoborophosphate and barium-sulfoborophosphate with chemical composition of $x\text{CaSO}_4\text{-}30\text{B}_2\text{O}_3\text{-(}70\text{-}x\text{)P}_2\text{O}_5$ and $x\text{BaSO}_4\text{-}30\text{B}_2\text{O}_3\text{-(}70\text{-}x\text{)P}_2\text{O}_5$ with $15 \leq x \leq 35$ mol% were prepared using melt quenching method. A series of glass samples doped with rare earth (RE = Dy_2O_3 , Sm_2O_3 and Eu_2O_3) with the chemical compositions of $25\text{CaSO}_4\text{-}30\text{B}_2\text{O}_3\text{-(}45\text{-}y\text{)P}_2\text{O}_5\text{-}y\text{RE}$ and $25\text{BaSO}_4\text{-}30\text{B}_2\text{O}_3\text{-(}45\text{-}y\text{)P}_2\text{O}_5\text{-}y\text{RE}$ with $0.1 \leq y \leq 1.0$ mol% were also prepared by melt quenching method. The amorphous phase of the 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 and Raman spectroscopy. The optical properties of glass samples were characterized by ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy and luminescence spectroscopy. The amorphous phase of the glass samples was confirmed by the diffuse broad XRD pattern. The infrared spectral measurements revealed the presence of vibrational groups of P-O linkage, BO_3 , BO_4 , P-O-P, O-P-O, S-O-B (sulfoborate network) groups and the bending B-O-B units in sulfoborophosphate structural network of glass samples. The Raman spectra also revealed the coexistence of structural units of BO_4 , SO_4^{2-} , PO_4^{3-} , and P-O-P in sulfoborophosphate glass samples. The luminescence spectra of Dy^{3+} ions doped glass samples exhibit four emission bands at around 482 nm, 572 nm, 662 nm and 685 nm, which correspond to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{9/2}$ transitions, respectively. The emission spectra of glass samples doped with Sm^{3+} ions show dominant peaks at around 559 nm, 596 nm, 642 nm and 709 nm which correspond to the transitions of ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$, ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$, ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ and ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{11/2}$, respectively. Meanwhile, glass samples doped with Eu^{3+} ions show emission spectra peaks around 589 nm, 611 nm, 651 nm and 701 nm which correspond to the transitions of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$, respectively. Absorption and emission spectra are used to evaluate the Judd-Ofelt intensity parameters and radiative transition probabilities, branching ratios and stimulated emission cross-sections of the three rare-earth ions (Dy^{3+} , Sm^{3+} , and Eu^{3+}) doped glass system. Based on this study, it can be concluded that the structural network features of calcium sulfoborophosphate and barium sulfoborophosphate glasses are similar, despite of different modifier. The incorporation of sulphate and rare-earth ions into the glass network show enhancement of chemical and physical stability, in addition to improving optical properties performance of the prepared glasses such as having high value of branching ratio, stimulated cross-section, gain bandwidth and optical gain. In view of this, calcium sulfoborophosphate and barium sulfoborophosphate glasses could be suggested as promising luminescent host material for solid-state lighting device application.

ABSTRAK

Sampel kaca tanpa dop kalsium sulfoborofosfat dan barium sulfoborofosfat dengan komposisi kimia $x\text{CaSO}_4\text{-}30\text{B}_2\text{O}_3\text{-(}70\text{-}x\text{)P}_2\text{O}_5$ dan $x\text{BaSO}_4\text{-}30\text{B}_2\text{O}_3\text{-(}70\text{-}x\text{)P}_2\text{O}_5$ dengan $15 \leq x \leq 35$ mol% telah disediakan melalui kaedah lindap-kejut leburan. Satu siri sampel kaca didop dengan nadir bumi (RE = Dy_2O_3 , Sm_2O_3 dan Eu_2O_3) dengan komposisi kimia $25\text{CaSO}_4\text{-}30\text{B}_2\text{O}_3\text{-(}45\text{-}y\text{)P}_2\text{O}_5\text{-}y\text{RE}$ dan $25\text{BaSO}_4\text{-}30\text{B}_2\text{O}_3\text{-(}45\text{-}y\text{)P}_2\text{O}_5\text{-}y\text{RE}$ dengan $0.1 \leq y \leq 1.0$ mol% telah juga disediakan melalui kaedah lindap-kejut leburan. Fasa amorfus sampel kaca telah dicirikan melalui kaedah pembelauan sinar-X (XRD), sementara ciri-ciri struktur sampel telah diukur menggunakan spektroskopi transformasi Fourier inframerah (FTIR) dan spektroskopi Raman. Sifat optik sampel kaca dicirikan melalui spektroskopi ultraungu-nampak-inframerah dekat (UV-Vis-NIR) dan spektroskopi luminesens. Fasa amorfus sampel kaca telah disahkan oleh corak XRD membur yang lebar. Pengukuran spektrum inframerah menunjukkan kewujudan kumpulan getaran P-O, BO_3 , BO_4 , P-O-P, O-P-O, S-O-B (rangkaian sulfoborat) dan unit pembengkokan B-O-B dalam rangkaian struktur sampel kaca sulfoborofosfat. Spektrum Raman juga menunjukkan kewujudan unit struktur BO_4 , SO_4^{2-} , PO_4^{3-} , dan P-O-P dalam sampel kaca sulfoborofosfat. Spektrum luminesens sampel kaca didop dengan ion Dy^{3+} mempamerkan empat jalur pancaran pada sekitar 482 nm, 572 nm, 662 nm dan 685 nm, yang masing-masing berpadanan dengan peralihan ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ dan ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{9/2}$. Spektrum pancaran bagi sampel kaca didop dengan ion Sm^{3+} menunjukkan puncak dominan pada sekitar 559 nm, 596 nm, 642 nm dan 709 nm yang masing-masing berpadanan dengan peralihan ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$, ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$, ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ dan ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{11/2}$. Sementara itu, sampel kaca didop dengan ion Eu^{3+} , menunjukkan puncak spektrum pancaran sekitar 589 nm, 611 nm, 651 nm dan 701 nm yang masing-masing bersesuaian dengan peralihan ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ dan ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$. Spektrum serapan dan pancaran telah digunakan untuk menilai parameter keamatan Judd-Ofelt dan kebarangkalian peralihan pancaran, nisbah cabangan dan keratan rentas pancaran rangsangan bagi tiga sistem kaca didop dengan ion nadir bumi (Dy^{3+} , Sm^{3+} , and Eu^{3+}). Berdasarkan kepada kajian ini, boleh disimpulkan bahawa ciri rangkaian struktur kaca kalsium sulfoborofosfat dan kaca barium sulfoborofosfat adalah sama walaupun berbeza pengubahsuai. Penambahan ion sulfat dan ion nadir bumi ke dalam rangkaian kaca telah meningkatkan kestabilan kimia dan fizik di samping meningkatkan prestasi sifat optik sampel kaca yang telah disediakan seperti mempunyai nilai yang tinggi bagi nisbah cabangan, keratan rentas rangsangan, jalur lebar gandaan dan gandaan optik. Oleh itu, kaca kalsium sulfoborofosfat dan kaca barium sulfoborofosfat boleh dicadangkan sebagai bahan hos pendaraahaya bagi aplikasi peranti pencahayaan keadaan pepejal.

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LIST OF ABBREVIATIONS

B_2O_3	-	Borate
$CaSO_4$	-	Calcium Sulfate
P_2O_5	-	Phosphorus Pentoxide
$BaSO_4$	-	Barium Sulfate
Dy_2O_3	-	Dysprosium Oxide
Eu_2O_3	-	Europium Oxide
Sm_2O_3	-	Samarium Oxide
Dy^{3+}	-	Dysprosium Ion
Eu^{3+}	-	Europium Ion
Sm^{3+}	-	Samarium Ion
f_{exp}	-	Experimental oscillator strengths
f_{cal}	-	Calculated oscillator strengths
IR	-	Infrared
S_{ed}	-	Electric dipole line strength
S_{md}	-	Magnetic dipole line strength
A_{rad}	-	Radiative transition probability
τ_{rad}	-	Radiative lifetime
β_r	-	Branching ratio
λ_p	-	Emission band position
FTIR	-	Fourier Transform Infrared
KBr	-	Potassium bromide
XRD	-	X-Ray Diffraction
UV	-	Ultraviolet
RE	-	Rare Earth
PL	-	Photoluminescence

LIST OF SYMBOLS

h	-	Planck's constant
$^{\circ}\text{C}$	-	Degree Celsius
ν	-	Frequency
c	-	Speed of light
$\alpha(\nu)$	-	Absorption coefficient
β	-	Nepheleuxetic ratios
Ω_2	-	Judd-Ofelt parameter
Ω_4	-	Judd-Ofelt parameter
Ω_6	-	Judd-Ofelt parameter
J	-	Total angular momentum
θ	-	Diffracted angle of the X-Ray beam
λ	-	Wavelength
n	-	Refractive Index

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CHAPTER 1

INTRODUCTION

This chapter outlines the fundamental background knowledge of the study. This includes the statement of research problem which led to the present research, objectives of the study, scope, significance of the research and outlines of the thesis.

1.1 Background of the Research

Glass is any solid that has an amorphous structure in nature and displays a glass transition when heated. Precisely, it is a solid formed by rapid melt quenching. It is hard, breakable and optically transparent. Diverse type of materials is used for making glass such as polymers, alloys of metals, aqueous solution, molecular liquids, ionic melts, etc. However, other elements are usually added to the ordinary glasses to change their physical and chemical properties.

The composition of materials used significantly contributes to the physical and chemical properties of glasses. Oxide glasses have three classes of components: the network formers, the intermediates, and modifiers. The network formers constitute a system of highly cross-linked chemical bond, while the intermediates and modifiers that are usually present as ions alter the network structure by being counterbalance by nonbridging oxygen atoms that are covalently bonded by the glass network (Saidu *et al.*, 2014).

In recent years, Lanthanide (Ln)-doped inorganic materials such as Ln-doped glasses, crystals and phosphors have gained rapid research interest due to their technological importance in the development of various optical and optoelectronic devices such as lasers, display devices, LEDs, fiber optic amplifiers and optical sensors (Srinivasulu *et al.*, 2013).

Borate (B_2O_3) is one of the essential glass forming oxides and has been incorporated into various kinds of glass system to attain the desired physical and chemical properties (Wan *et al.*, 2014). Borate glasses have been of scientific interest for many years because of their potential applications like electro-optic switches, electro-optic modulators, solid-state laser materials and non-linear optical parametric converters. It possess excellent transparency, thermal stability and excellent rare earth ion solubility but it has higher phonon energy ($\approx 1300\text{ cm}^{-1}$) which reduces the rare earth emission intensity due to their higher nonradiative decay (Swapna *et al.*, 2013). The structure of vitreous B_2O_3 consists of a random network of boroxol rings and BO_3 triangles connected by B-O-B linkages. However, metal oxides like MgO, CaO, SrO, BaO, ZnO and Al_2O_3 , etc. have been added to B_2O_3 and were found to be excellent stabilizers of borate glasses (Sumalatha *et al.*, 2013).

Phosphate (P_2O_5) is another good glass forming oxides due to their favourable properties such as reasonably low liquid and glass transition temperatures, low viscosity, high thermal expansion coefficient, high electrical conductivity and high ultraviolet transmission, it's found application in a wide range of fields. For example, phosphate glasses are used in lasers, a solid electrolyte, bio-medical devices and nuclear waste immobilization (Joseph *et al.*, 2015). However, practical forming characteristics of phosphate glasses is limited because of their hygroscopic nature and relatively poor chemical durability (Jha and Jayasimhadri, 2016).

Therefore, to overcome the difficulties and limitations of both borate and phosphate glasses, the two host are combined to form a new glassy material called "Borophosphate glass" which gives a better advantageous as they exhibit different properties. However, borophosphate glasses are promising host materials for optical applications because of their excellent optical properties, low refractive indices, low dispersion and good transparency from ultraviolet to the near-infrared regions. Furthermore, the combination of B_2O_3 and P_2O_5 in the same matrix with additional oxides resulted in properties enhancements (Wan *et al.*, 2014). The role played by B_2O_3 and P_2O_5 in the glass structure, and the interaction with other elements in the glass network is an interesting subject of glass science. Hence, the combination of

the two network formers enables considerable modifications of the properties of the materials compared to pure borate and phosphate networks alone (Pang *et al.*, 2014). For instance, the chemical durability can be increased, or volume nucleation can be controlled by mixing the borate and phosphate groups.

Borophosphate along with modifiers (sulfate) is a fascinating area of study. In these glasses, the basic units of pure borate glasses are trigonal BO_3 groups, whereas those of pure phosphate glasses are PO_4 tetrahedra linked through covalent bridging oxygen. The addition of a modifier to borate and phosphate networks has different effects. In borate network, the addition of a modifier in some concentration ranges increases the degree of polymerization. The boron coordination changes from trigonal (BO_3) to tetrahedral (BO_4), whereas in phosphate network, an ultra-phosphate network consisting of Q^2 and Q^3 tetrahedra may form with $\text{O/P} < 3.0$ (Ravi Kumar *et al.*). However, in the development of glass material, the stability and efficiency can be tailored by introducing a modifier.

Calcium oxide and barium oxide are two useful modifiers in modifying the phosphate properties (Li *et al.*, 2016). Calcium oxide and barium oxide served as a modifier to reduce the hygroscopic properties while sulfur was added into borophosphate as intermediate to enhance the host network. The influence of calcium oxide on iron phosphate could improve glass chemical durability, especially the alkaline resistance of glass fibre reinforced concrete (Brow, 2008). Barium oxides work as the modifier that could strengthen the glass network, restraining glass from crystallization, leading to P-O-Ba bands and improving the glass thermal stability, low melting temperature and wide glass forming region (Lu *et al.*, 2015). Moreover, as a divalent network modifying oxide, BaO increases density, refractive index and vitreous luster of the glass, slightly promote the melting process and enhance the ability to absorb radiation (Lu *et al.*, 2015).

Rare earth (RE) doped glasses have become an important class of optical systems due to their applicability as a solid-state laser, waveguides lasers and optical amplifiers. Most of the studies of glasses focus on explaining the structure properties regarding non-bridging oxygen (NBO) and boron coordination number and a few

studies were concerned about understanding the role of rare earth doping in the structure of glasses (Dias *et al.*, 2016).

Luminescence intensity and lifetime of Ln³⁺ ions in glasses would depend on the excitation wavelength, environment, symmetry or nature of ligands, i.e., the covalence between rare earth ions and the ligands around them and cross-linking of the f-f transitions (Dias *et al.*, 2016). Thus, borophosphate-based glasses are expected to be a promising host material for RE ions because of its excellent optical properties, low refractive indices, low dispersion and good transparency from the ultraviolet to the near-infrared regions (Yao *et al.*, 2017).

Among the trivalent Lanthanide: Eu³⁺ ions are found to be an essential ion to probe deep into the local environment around RE³⁺ ions in different matrices and to have the potential applications. This useful information about the local structure around Eu³⁺ ions can be obtained quite easily from its f-f transition spectra. In Eu³⁺ ions, the ground state ⁷f₀ level and the first excited ⁵D₀ level are non-degenerate (J=0) under any symmetry and the local environment of Eu³⁺ ions depends only on the splitting of ⁵D₀ → ⁷f_j (J = 0-4) transitions (Hima Bindu *et al.*, 2016). Among all the rare earth ions, Eu³⁺ doped borate materials are prepared as red luminophores for display applications as well as for red LED's due to the host matrix chemical, mechanical durability and broad spectral transparency (Swapna *et al.*, 2014).

Furthermore, the trivalent europium ions are well-established as a spectroscopic probe to get an insight into the structure and nature of chemical bonds. This is mainly because of the simple energy level scheme of Eu³⁺ ions and the site-selective nature of intensities between ⁷f_j and ⁵D₀ energy levels. Also, the relative variation of emission intensities within the orange-red region due to site-selective nature of hypersensitive and non-hypersensitive ⁵D₀ → ⁷f_j and ⁷f₂ transitions are of particular interest for device applications (Swapna *et al.*, 2014).

Sm³⁺ ions containing glasses are fascinating to study due to strong luminescence and high quantum efficiency of the ⁴G_{5/2} level. Therefore, glasses doped with Sm³⁺ ions have attractive applications as optical devices (e.g., optical

data storage, colour displays e.t.c.) (Ramteke *et al.*, 2015). Sm^{3+} ions give very strong fluorescence in the orange-red spectral region in a variety of lattices, leading to potential high-power lasers, both in compact fiber and planar geometries. But only a few attempts have been made to explore the possibility of using orange-red luminescence of Sm^{3+} ions for the development of LED's in the visible spectral region as well as visible optical devices such as visible lasers and fluorescent devices.

Basavapoornima and Jayasankar (2014) noted that the main reason for not conducting several spectral studies on Sm^{3+} ions doped in glasses is connected to its $4f^6$ complicated structure. Many energy levels lying close to each other interpret the absorption spectrum of this ion somewhat tricky for the determination of essential intensity parameters needed in the calculation of various radiative properties which otherwise require a suitable and skilful calculation technique.

Dy^{3+} ion is another promising rare earth ion for white light applications due to the transitions between $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ energy levels corresponding to the dominant emission bands at blue and yellow region respectively. The $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ emission band is due to the electric dipole transition and is profoundly affected by the ligand field and the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ emission is due to magnetic dipole transition (Vijayakumar *et al.*, 2014). The linked between a blue and yellow region in CIE 1931 chromaticity diagram usually passes through the white light region. Furthermore, white light can be produced from the glass materials by adjusting the yellow to blue (Y/B) intensity ratio by varying the glass composition, RE ion concentration and excitation wavelengths (Vijayakumar *et al.*, 2014).

The optical homogeneity of glassy matrices makes available RE ions to exhibit different latent laser transitions. Spectroscopic study of RE ions in glasses suggests information with considering transition probabilities, lifetimes, branching ratios of excited states, which are vital in the design and growth of various electro-optic and optical devices. To understand the quantitative optical phenomena of rare-earth ions in glasses, it is essential to evaluate radiative and non-radiative decay process of related $4f$ levels. The Judd-Ofelt theory parameterizes the induced electric

dipole transitions. The intensity of induced electric dipole transitions can be described regarding three phenomenological intensity parameters Ω_λ ($\lambda = 2, 4, 6$). The Judd-Ofelt theory is usually adopted to obtain the radiative transition probabilities including emission by utilizing the data of absorption cross section of several f-f electric dipole lines. The physical and chemical implement of three Ω_λ parameters ($\lambda = 2, 4, 6$) is becoming more evident by combining information of the local ligand field of doped ions by other spectroscopic technique and give the information about the rare-earth environment in glass such as bond covalency and symmetry. The non-radiative decay rate can be evaluated experimentally by combining the lifetime measurements, which includes contributions of multiphoton decay, energy transfer such as cross relaxation and frequency up conversion properties of rare earth doped glasses (Madhukar Reddy *et al.*, 2015).

Selection of borophosphate glass in this study as a glass former is due to they provide interesting optical and structural properties such as low refractive indices, low dispersion and good transparency from the ultraviolet to the near-infrared regions (Yao *et al.*, 2017). An exciting characteristic of borate glasses is the appearance of variations in its structural properties when different modifier oxides are introduced. The addition of alkali earth metal into the glass structure leads to disruption of the glass network and promotes the formation of non-bridging oxygen groups, which is in contrast to alkaline earth oxides (Balakrishna *et al.*, 2017).

Therefore, due to the increasing demands on the distinct types of visible lasers and light sources. Also, the studies of these rare-earth ions' materials have become an interesting topic in the field of material science because of its essential properties, so, more findings need to be done to determine the efficiency of rare earth in new material.

1.2 Problem Statements

The problem confronting phosphate glasses research is the hygroscopic and volatile nature of most metaphosphate, ultra-phosphate and polyphosphate materials.

Furthermore, phosphate glasses have limitations in their optical performance. However, improving the optical performance for a new efficient luminescent material remained the most challenging task in the industry for solid-state laser applications. Therefore, the incorporation of sulphate ions into the phosphate network improved the rare earth optical performance of borophosphate glasses. Furthermore, lasers are based on specific active materials that needs to satisfy good doping levels. Therefore, an effort on new materials and new dopants concentrations is required to achieve progress in the field. The Judd-Ofelt parameters, radiative properties, optical properties, physical properties, luminescence properties and structural features of RE (Dy^{3+} , Sm^{3+} and Eu^{3+}) doped calcium sulfoborophosphate glass and barium sulfoborophosphate glass are rarely investigated. Additionally, since there is a lack of report on these glasses, it is of important to study these glasses in order to give more information on the influence of Dy^{3+} , Sm^{3+} and Eu^{3+} ions on the glasses.

1.3 Objectives of the Research

The main objective of this research is to develop a new luminescent host material that can exhibit a substantial enhancement of the optical and luminescence properties via doping of calcium sulfoborophosphate glass and barium sulfoborophosphate glass with different concentrations of Dy^{3+} , Sm^{3+} and Eu^{3+} ions. The specific objectives of this research are:

- (a) To determine and compare the influence of doped Dy^{3+} , Sm^{3+} and Eu^{3+} of different concentration on calcium sulfoborophosphate glass and barium sulfoborophosphate glass in terms of their structural features and regarding their luminescence characteristics enhancements.
- (b) To analyze and compare the impact of emission and absorption data between calcium sulfoborophosphate glass and barium sulfoborophosphate glass doped varies concentrations of Dy^{3+} , Sm^{3+} and Eu^{3+} in terms of radiative properties using Judd-Ofelt analysis.

1.4 Scopes of the Research

- (a) In this study, the samples of undoped calcium sulfoborophosphate glass and barium sulfoborophosphate glass with the chemical composition of $x\text{CaSO}_4-30\text{B}_2\text{O}_3-(70-x)\text{P}_2\text{O}_5$ with $15 \leq x \leq 35$ mol% and $y\text{BaSO}_4-30\text{B}_2\text{O}_3-(70-y)\text{P}_2\text{O}_5$ with $15 \leq y \leq 35$ mol% were prepared by conventional melt quenching method. The series of glass samples doped with rare earth (RE = Dy_2O_3 , Sm_2O_3 and Eu_2O_3) with the chemical compositions of $25\text{CaSO}_4-30\text{B}_2\text{O}_3-(45-x)\text{P}_2\text{O}_5 - x\text{RE}$ with $0.1 \leq x \leq 1.0$ mol% and $25\text{BaSO}_4-30\text{B}_2\text{O}_3-(45-y)\text{P}_2\text{O}_5 - y\text{RE}$ with $0.1 \leq y \leq 1.0$ mol% were also been prepared by conventional melt quenching method.
- (b) The amorphous nature of the glass sample was ascertained by X-ray Diffraction (XRD) and thermal stability of the undoped prepared glass samples were determined using Differential Thermal Analyzer (DTA).
- (c) The structural features of the host materials are investigated using Infrared and Raman spectroscopic techniques and excitation, emission and absorption of (RE= Dy^{3+} , Sm^{3+} and Eu^{3+}) doped calcium sulfoborophosphate glass and barium sulfoborophosphate glass were determined using photoluminescence and ultraviolet visible spectroscopy respectively.
- (d) The optical absorption parameters like optical band gap, refractive index, electronic polarizability and Urbach energy are measured from the data of UV-Vis spectroscopy.
- (e) The radiative parameters on the luminescence properties of (RE= Dy_2O_3 , Sm_2O_3 and Eu_2O_3) doped calcium sulfoborophosphate glass and barium sulfoborophosphate glass were determined using Judd-Ofelt theory.

1.5 Significance of the Research

Glasses are exceptionally significant optical materials. The rapid development of laser research has led to get much attention about theoretical treatment of RE ions in glass compare to other luminescence center. Conducting details and comprehensive research on the proposed glass host samples and the rare earth ions as dopant would contribute in perspective and investigative studies regarding their structural and optical properties of the glass samples. The Judd-Ofelt results provides information on the absorption and emission of the newly luminescence host. The new material can, therefore, provide a baseline data for future research and can be used as an alternative material for solid-state laser applications such as colour displays, optical fibre and amplifiers.

1.6 Outlines of Thesis

This thesis is classified into five different chapters. Chapter 1 describes the background of the research, problem statement, objective of the research, outlines of the thesis and significance of the research aimed to highlight the introduction aspect of the research work. In Chapter 2, an extensive literature review regarding the host structure used in the current study were made. The review includes description of structural features, luminescence properties as well as Judd-Ofelt and radiative parameters of other host materials. Chapter 3 describes the experimental procedures which encompass the methodology in preparing the glass samples with the analytical techniques used. Furthermore, detailed information about the types of spectroscopic methods used and the working principle of X-ray diffraction (XRD), FTIR and Raman spectroscopy, luminescence and UV-Visible-NIR spectrometer. Chapter 4 presents the results and discussion regarding the different characterization, measurements and evaluations of the prepared samples. Chapter 5 presents the conclusions and recommendations for future work based on the research vacuums acknowledge during this study.

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