PHYSICAL AND SPECTROSCOPIC PROPERTIES OF LITHIUM-BOROSULFOPHOSPHATE GLASSES DOPED WITH DYSPROSIUM AND EUROPIUM IONS

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Specially dedicated to Almighty God, who gave me strength and wisdom to have undergone this programme and to the loving memory of my late mother

Mrs.Lami I. Dogo

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ABSTRACT

A study had successfully been conducted on lithium-borosulfophosphate glasses to examine the effect of dysprosium and europium ions upon their physical and spectroscopic properties. The glass samples were synthesized via convectional melt quenching technique and characterized using density, X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), UV-Vis-NIR, and Photoluminescence (PL) measurements. The amorphous nature of the glass was confirmed using XRD studies. It is observed that the physical and optical properties of these glasses are found to be strongly influence by varying the glass composition. The glass density and refractive index increase proportionally with Dy_2O_3 and Eu_2O_3 concentration whereas the molar volume exhibits opposite behaviour. The result from FTIR spectra analysis indicates the presence of BO_3, BO_4, PO_4 and SO_4^{2-} groups in the host network structure. UV-Vis-NIR spectra of Dy^{3+} doped glass samples recorded seven absorption peaks while on the contrary, Eu^{3+} doped glass samples exhibits four peaks in UV-Visible region and two peaks in NIR region. The optical band gap was found to decrease gradually with increase in Dy^{3+} and Eu^{3+} concentration while the Ubach's energy shows inverse trend. Meanwhile the negative and positive value of the bonding parameters confirmed the corresponding ionic and covalent nature of Dy−O and Eu−O ligand bond in the host matrix. The luminescence spectra for Dy^{3+} doped samples at the excitation wavelength of 386 nm revealed two intense emission peaks at 494 nm ($^4F_{9/2}\rightarrow{}^6H_{15/2}$), 585 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) and a very weak peak at 673 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$). Conversely, doping the samples with Eu^{3+} ions gives rise to four emission peaks at 587 nm ($^5D_0\rightarrow{}^7F_1$), 612 nm ($^5D_0\rightarrow{}^7F_2$), 650 nm ($^5D_0\rightarrow{}^7F_2$) and 698 nm ($^5D_0\rightarrow{}^7F_4$) under the excitation wavelength of 394 nm. The superior features shown by the current glass material as a result of good correlations between the host network and dopant ions specifies its potentialities for lighting device applications.

ABSTRAK

Satu kajian telah berjaya dijalankan pada sistem kaca lithium-borosulfophosphate untuk menentukan pengaruh ion-ion dysprosium dan europium ke atas sifat-sifat fizikal dan spektroskopi. Sampel kaca telah di sintesis melalui teknik pencairan sepuh lindap lazim dan pencirian dengan menggunakan pembeluan sinar-X (XRD), infra merah transformasi Fourier (FTIR), UV-Vis-NIR dan fotoluminescens (PL) spectroskopi dan pengukuran ketumpatan. Sifat amorfus kaca telah ditentusahkan menggunakan kajian XRD. Dapat diperhatikan bahawa sifat-sifat fizikal dan optik kaca yang disediakan didapati sangat dipengaruhi oleh komposisi kimia yang digunakan. Ketumpatan dan indeks biasan kaca meningkat berkadaran dengan kepekatan Dy_2O_3 dan Eu_2O_3 manakala isipadu molar menunjukkan sifat yang bertentangan. Keputusan dari análisis IR spektrum menunjukkan kewujudan kumpulan BO_3, BO_4, PO_4 dan SO_4^{2-} dalam struktur rangkaian hos. UV-Vis-NIR spektrum bagi sampel kaca dop Dy^{3+} menunjukkan terdapat tujuh puncak penyerapan manakala sebaliknya bagi sampel kaca dop Eu^{3+} menunjukkan empat puncak dalam julat UV boleh nampak dan dua puncak dalam julat NIR. Jurang jalur optik didapati menurun secara beransur-ansur menurut peningkatan kepekatan Dy^{3+} dan Eu^{3+} manakala tenaga Ubach pula menunjukkan sifat yang bertentangan. Sementara itu parameter ikatan telah memberikan nilai negatif dan positif yang menunjukkan sifat ionik dan kovalen dalam sampel yang sepadan dengan ikatan ligan Dy−O and Eu−O dalam matriks hos. Spektrum luminescens bagi sampel dop Dy^{3+} dengan panjang gelombang pengujaan pada 386 nm telah menunjukkan dua puncak pancaran yang tinggi pada 494 nm ($^4F_{9/2}\rightarrow{}^6H_{15/2}$), 585 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) dan satu puncak yang sangat lemah pada 673 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$). Sebaliknya, sampel dop Eu^{3+} ion telah menunjukkan empat puncak pancaran pada 587 nm ($^5D_0\rightarrow{}^7F_1$), 612 nm ($^5D_0\rightarrow{}^7F_2$), 650 nm ($^5D_0\rightarrow{}^7F_2$) dan 698 nm ($^5D_0\rightarrow{}^7F_4$) dengan pengujaan pada panjang gelombang 394 nm. Ciri-ciri yang telah diperolehi dari sampel kaca yang dihasilkan telah menunjukkan bahawa terdapat hubungan yang menarik diantara rangkaian hos dan ion dopan yang digunakan dan menunjukkan potensi untuk digunakan dalam laser dan peranti pencahayaan.

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B_2O_3	-	Borate
Dy_2O_3	-	Dysprosium oxides
Dy^{3+}		Dysprosium ion
Eu_2O_3	-	Europium oxides
Eu^{3+}		Europium ion
FTIR		Fourier Transform Infrared
H_2O		Water
H_2SO_4	-	Sulfuric Acid
H_3BO_3	-	Boric Acid
H_3PO_4	-	Phosphoric Acid
IR		Infrared
KBr		Potassium bromide
Li_2CO_3		Lithium Carbonate
Li_2O		Lithium oxides
NIR		Near Infrared
P_2O_5	-	Phosphate
PL		Photoluminescence
SO_3	-	Sulfur oxides
UV		Ultraviolet
XRD		X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter outlines the pertinent introduction covering the basic background knowledge of the study and some reviews from previous researched. It include the problem statement which led to this research, objectives of study, scope of study, significance of study and the layout of the dissertation.

1.2 Research Background

The word glass is derived from a latin term "Glasseum" which means lustrous and transparent materials. In 1949, American Society for Testing Materials (ASTM) defined glass as an inorganic product of fusion that is cool to a rigid condition without crystallization (Stanworth, 1946). In this context, a glass is amorphous material which can be obtained by various techniques namely melt-quenching, sol-gel, chemical vapour decomposition process, etc (Rao et al., 2016). Regarding the structural orientation, glassy materials have short range arrangement, but not symmetric, lack of uniformity, and have no long range periodically which yielded fairly random structure unlike crystal with a well-defined structure and atoms arranged in three dimensional periodic. Hence, instead of crystalline sharp peaks a single broad hump (noise) is seen in the X-ray diffraction patterns of a glass.

The study of the physical and spectroscopic properties of glasses is of great significant because it gives an insight into the fundamental process-taking place in them. Categorically, the physical properties of the glasses are to a large extent controlled by the structure, composition and the nature of the bonds of the glasses. The research of the changes in the physical and spectroscopic properties of glasses via suitable controlled of chemical composition, doping etc., is of considerable interest in the application perspective. These materials have potential applications as laser materials, memory devices, optical amplifiers, and modulators, photonics devices for communications, advance computer applications and as semiconducting devices (Campbell and Suratwala, 2000.)

Currently, much more attention has been paid to phosphate glasses among the various types of glasses due their tremendous applications in many emerging technologies such as solid-state lasers, nonlinear optics, biosensors, colour filters, radioactive waste storage, photonics and biomedical engineering etc (Elisa et al., 2013). Phosphate glasses are technologically important materials because they posses some superior physical properties such as high thermal expansion coefficient, low melting temperature, low softening temperature and high electrical conductivity. Unfortunately, poor chemical durability and hydroscopic nature of these glasses discourage their further development and limit their practical applications. Hence, addition of trivalent alkaline oxide has proven to enhance their chemical stability (Das et al., 2006).

Borate (B_2O_3) is another good glass former and flux material that usually incorporates with other modifier oxide to improved its physical and chemical behaviour. Borate glasses are known to have significant properties which include low melting temperature, good thermal stability, lower degree of expansion in volume to the change in temperature, high refractive index and are being used in modern industry for different purposes like lead borates in plasma soldering, sodium resistance and aluminium borates glasses in sodium discharge lamps, lithium borates in optical lenses (Anjaiah et al., 2014). Borate glasses constitute an interesting system, which the network building unit can be either borate triangles (BO_3) with non-bridging oxygen atoms or borate tetrahedrons (BO_4) with all bridging oxygen atoms. These glasses can easily be melted, owning smaller mass compare to other glass network former, chemically durable and thermally stable. Besides, they are high transparency and acted as a good host for transition metal ions and rare earth ions making them suitable for optical materials. Hence, hydroscopic properties and the high phonon energy of B_2O_3 are considered as a drawback to the glass industry (Vijayakumar et al., 2015).

However, to overcome the individual limitations of phosphate and borate glass, the two network formers are combined to form a new glassy material called "Borophosphate glass" which offers greater advantageous as they exhibit different properties (Wong et al., 2014). The presence of P_2O_5 in the borate glasses can enhance the glass quality when modified with rare earth ions (Tonchev et al., 2015). Pang et al. (2014) reported that borophosphate glasses have acceptable chemical durability compared to pure borate and pure phosphate and has drawn the attention of researchers due to their potential applications in optical technology. In addition, the efficiency and stability of borophosphateglass can be tailored by introducing a modifier. Many researchers have well known that lithium is more electropositive ion. Addition of lithium as modifier to the glass network can change the glass lattice, open up the network structure, lower the viscosity, and weaken the bond strength of the glass there by improving the glass stability (Shen et al., 2015)

Quiet recently, Kumar et al. (2012a) introduced sulfate into borophosphate forming "Borosulfophosphate glasses" to further enhance the strength of the host matrix. These materials exhibit better features than borophosphate glasses such as high electrical conductivity compatible with the electrode materials, low strain birefringence, wide flexibility of chemical composition, and easy preparation on large scale, low melting point, low optical loss, low non-linear refractive index coefficient, superior refractory nature, thermally and chemically stable. Unluckily, the efforts towards understanding the optical and luminescence properties of borosulfophosphate doped glass materials was only restricted to the transition metal ions.

Furthermore, glasses activated with rare earth ions have been identified as a good luminescence host materials which convert an incident energy input into emission of electromagnetic waves in the ultraviolet (UV), visible (VIS), or infrared (IR) regions of the spectrum. The emission of the rare doped materials correspond to the 4f-4f and 4f-4d electronic transitions which is due to the shielding effect from the outer orbital (5s and 5p) on the 4f electrons and hence gives high emission efficiency from the ultraviolet to the infrared regions (Janek et al., 2016)

Over the past few decades, much attention has been focused towards dysprosium and europium ions doped glass materials for the development of optical devices such as solid-state lasers and lighting devices, fiber amplifiers and infrared to visible up-converters (Murugasen et al., 2015). To date, these materials become an interesting topic in the field of material science and therefore need to be further explore.

1.3 **Problem Statement**

The increasing demand for new efficient luminescent glass materials is the key issue in laser lighting technology. Although few researchers have identified borosulfophosphate glasses as the most favourable and special luminescent host matrix owning to their notable properties and derivations in myriads of potential applications for the development of solid-state lasing and lighting devices (Kiran and Kumar, 2013, Kumar et al., 2012c), yet the physical and structural features of borosulfophosphate glasses are not fully understood. Furthermore, the effect of Dy^{3+} and Eu^{3+} ions on the optical and luminescence properties of lithium-borosulfophosphate glasses to the best of our knowledge has not been reported. Therefore, the present study aim to investigate the influence of varying concentration of Dy^{3+} and Eu^{3+} ions on the physical and spectroscopic (viz, structural, optical and luminescence) properties of lithium-borosulfophosphate glasses.

1.4 Objectives of the Study

This study embarks on the following objectives:

- To determine the influence of varying concentration of dysprosium and europium ions on the physical and structural properties of lithium-borosulfophosphate glasses
- To determine the effects of different concentration of dysprosium and europium ions on the optical and luminescence properties of lithium-borosulfophosphate glasses

1.5 Scope of the Study

In this study, the preparation of lithium-borosulfophosphate glasses doped with different concentration of dysprosium and europium ions based on the composition of $15Li_2O$-$30B_2O_3$-$15SO_3$-$(40\text{-}x)P_2O_5$-xDy_2O_3 and $15Li_2O$-$30B_2O_3$-$15SO_3$-$(40\text{-}x)P_2O_5$-xEu_2O_3 (where x = 0.1, 0.3, 0.5, 0.7 and 1.0 in mol%) by melt-quenching method is the key focus. Sulphur oxide was incorporated into borophosphate as intermediate to enhance the host network whereas lithium oxide was used as modifier to reduce the hydroscopic properties. Dy^{3+} and Eu^{3+} ions were chosen to be dopant ions in order to investigate the effect of dopant on the optical and luminescence properties. Different types of measurements were used. The glass density was measured via Archimedes method to examine the physical properties while the X-Ray Diffraction (XRD) was employed to indentify the phase of the obtained samples. Fourier Transform Infrared (FTIR) spectroscopy on the other hand, was used to determine the structural features of host material. The UV-VIS-NIR was used to determine the absorption spectra, which are useful for determination of optical energy band gap, Urbach's energy and other optical parameters. A luminescence study was performed on the glass samples in order to study the effect of varying concentration of dysprosium and europium ions on the excitation and emission spectra.

1.6 Significances of the Study

The current study has been carried out to understand further the structural information, physical, optical and luminescence properties of glass. However, doping the samples with Dy^{3+} and Eu^{3+} may develop new luminescence materials. Furthermore, the study on optical and luminescence properties in this work is significant in providing a baseline data that can be used for further research and development of luminescent host material for solid-state lighting devices.

1.7 Dissertation Layout

The content of this dissertation is divided into five chapters. Chapter 1 presents the background knowledge of the study and some reviews from previous studies related to borosulfophosphate glass materials. It describes the problem statements, which led to this research, objectives of study, scope of study, significance of study and the dissertation layout, are also presented in this chapter. Chapter 2 covered the definition, glass formation and physical properties of glass. General descriptions and the concise review regarding the host structure used in this work are provided. The theoretical perspective of physical and optical parameters is also discussed. However, the previous studies of Dy^{3+} and Eu^{3+} doped glass system on the optical and luminescence properties are reported. The concise background of characterization techniques and the detailed experimental procedures of our research are documented in Chapter 3. Chapter 4 deals with the discussion based on experimental results obtained from chapter 3. The result on the XRD pattern, density measurement, FTIR vibrational spectra, absorption spectra, excitation and emission spectra along with figures and tables are discussed in this chapter. Chapter 5 concludes this dissertation with a brief summary on the achievement of the objectives. Recommendation for future studies is also presented in this chapter.

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