STRUCTURAL AND LUMINESCENCE PROPERTIES OF ZINC ANTIMONY BOROPHOSPHATE GLASS DOPED WITH RARE-EARTH IONS

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

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To my beloved family thanks for the prayer, love and patience.
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ABSTRACT

A quaternary system of borophosphate glasses formulated with zinc and antimony were prepared in three series, namely series A, series B and series C. All the samples in each series were prepared using melt quenching technique followed by annealing at 350°C for 1 hour. The best composition in Series A [10P₂O₅–40B₂O₃–(50–x)Sb₂O₃–(x)ZnO] (10 ≤ x ≤ 50) in terms of stability and transparency, was selected for preparation of Series B [10P₂O₅–40B₂O₃–40Sb₂O₃–10ZnO–1 RE] (RE=Sm³⁺/Eu³⁺/Er³⁺/Nd³⁺), in order to study the effect of the different dopand ions to the molecular structure and luminescent properties of the glass system. Series C of [10P₂O₅–40B₂O₃–40Sb₂O₃–10ZnO–(x)Sm₂O₃] (0.5 ≤ x ≤ 2.0) was prepared to study the effect of samarium concentration on the luminescence properties. The XRD results showed that the crystalline phase of the glass changed with different amount of zinc and antimony substitution. Crystalline phase was observed for sample containing more than 30 mol % of zinc oxide. Result of IR spectroscopy indicated that ZnO affected the basic coupling units of P-O bond and Sb³⁺ ions entered the glass system by breaking up the B-O-B bonds. The modification of zinc antimony borophosphate glasses with rare earth was studied and showed that the presence of rare earth ion in the glass system did not change the structural features. Among various rare earth, Eu³⁺ and Sm³⁺ showed the strongest luminescence intensity. The luminescence intensity of Sm doped glass changed in no specific pattern when the concentration, x increased from 0.5 to 2.0 mol %. The samarium doped glass showed intense luminescence with a very sharp peak dominated by the ⁴G₅/₂ → ⁶H₇/₂ transition at 590 nm.
ABSTRAK

Sistem kuatenari bagi kaca borofosfat yang diformulasikan dengan zink dan antimoni telah disediakan dalam tiga siri, iaitu siri A, siri B dan siri C. Kesemua sampel dalam setiap siri disediakan melalui kaedah peleburan kaca dengan rawatan haba pada suhu 350°C selama 1 jam. Komposisi terbaik dalam siri A \([10P_2O_5–40B_2O_3–(50-x)Sb_2O_3–(x)ZnO]\) (10 ≤ x ≤ 50) dari segi aspek kestabilan dan lutsinar, dipilih bagi penyediaan siri B \([10P_2O_5–40B_2O_3–40Sb_2O_3–10ZnO–1 Nadir Bumi]\) (Nadir Bumi=Sm\(^{3+}/Eu\(^{3+}/Er\(^{3+}/Nd\(^{3+}\)), untuk mengkaji kesan jenis dop yang berbeza ke atas struktur molekul dan sifat luminesen sistem kaca tersebut. Siri C \([10P_2O_5–40B_2O_3–40Sb_2O_3–10ZnO–(x)Sm_2O_3]\) (0.5 ≤ x ≤ 2.0) telah dipilih bagi mengkaji kesan perubahan kepekatan samarium terhadap sifat luminesen kaca. Keputusan XRD menunjukan terdapat perubahan fasa kristal apabila terdapat perubahan pada jumlah zink dan antimoni. Fasa kristal dapat diperhatikan bagi sampel yang mengandungi lebih daripada 30 mol % zink oksida. Keputusan spektroskopi IR menunjukkan bahawa ZnO memberi kesan kepada ikatan unit pasangan asas P-O dan ion Sb\(^{3+}\) memasuki sistem kaca dengan memutuskan ikatan B-O-B. Pengubahsuaian kaca borofosfat zink antimoni dengan nadir bumi telah dikaji dan keputusan menunjukkan kehadiran ion nadir bumi dalam sistem kaca tidak mengubah ciri strukturnya. Antara nadir bumi tersebut, Eu\(^{3+}\) dan Sm\(^{3+}\) menunjukan keamatan luminesen yang tinggi. Keamatan luminesen bagi kaca yang didop dengan Sm berubah dengan corak yang tidak spesifik apabila kepekatan, x diubah daripada 0.5 ke 2.0 mol %. Kaca yang didop dengan samarium menunjukkan luminesen yang kuat dengan puncak yang sangat tajam didominasi oleh peralihan \(^{4}G_{5/2} \rightarrow ^{6}H_{7/2}\) pada 590 nm.
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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The first step to understand about glass is by the definition. Progress in research and development process makes the definition of glass changes continuously. The scope of the definition becomes wider in terms of ideas and perspective. The definition given by the researchers mostly focuses on the method of preparation and the glass structure. Scagliotti et al., (1987) defined glass as an inorganic product of fusion which has cooled to a rigid condition without crystallization and obtained by a melt-quenching process.

There are many types of glass such as oxide glass, halide glass, chalcogenide glass and silicate glass. For optical application, oxide glass gives numerous advantageous compare to other glasses. Phosphate (P$_2$O$_5$), borate (B$_2$O$_3$), germinates (GeO$_2$) and silicate (SiO$_2$) glasses are the important examples of oxide glasses. Due to the different structures and properties, some of the glasses can easily react with atmospheric moisture and degrade by their own hygroscopic nature.
Among the different types of glasses, phosphate based glasses show several advantageous due to their low melting and glass transition temperatures. Phosphate glasses offer wide application as laser host, glass to metal seals and bio compatible material (Kirkpatrick et al., 1995). Alkali phosphate glasses can be used as fast ion conductors, optical switches, waveguides and fibers. The high thermal expansion coefficient and glass transition temperature makes phosphate glasses suitable for application in solid state batteries and electrolytes (Das et al., 2006).

Despite of many possible applications in various areas of technology, there are limited studies reported on phosphate glasses. This is may be due to their poor chemical durability and low thermal stability. Obviously, the low chemical durability makes these glasses have limited applications. But, however the addition of divalent and trivalent alkali oxide has proven to improve their chemical durability (Das et al., 2006).

Recently, an intensive study on borate glass has been conducted for scientific and technological demand. The properties of borate glass such as high sensitivity and low cost preparation offer better prospect especially for thermoluminescence application. Borate doped rare earth ions attracts more attention because of the great color coordinate and low thermal degradation. These glasses have been reported to have high luminescence properties and improved optical and electrical properties (Ivankov et al., 2006).

In addition, borate glasses are great hosts for glass system because they can accommodate large concentrations of active ions. Similarly with phosphate glass, fundamental investigation of glass structure also can be conducted using borate due to a large range of glass forming compositions (Kamitsos and Chryssikos, 1991).
There are some important range of compositional possibilities for borate such as metaborate, pentaborate, orthoborate, diborate, and pyroborate. The basic unit of pure amorphous borate glasses is trigonal BO$_3$ groups and for pure phosphate glasses is PO$_4$ tetrahedra that linked through covalent bridging oxygen (Gaafar et al., 2008).

Unfortunately, as a glass network former, phosphate and borate alone is not a stable compound due to the chemical durability limitation. This restrain can be improved and stabilized by the incorporation of other network former. For example, the stability of phosphate glass can be improved by introducing the boron oxide into the structural network.

Park et al., (2010) reported that borophosphate glasses have acceptable chemical durability compared to pure borate and pure phosphate. The combination of two glass formers, P$_2$O$_5$ and B$_2$O$_3$ possesses a variety of other useful properties. In fact, the presence of P$_2$O$_5$ in the borate glasses can improve the glass quality when modified with rare earth ions (Rayappan et al., 2010).

The combination of these two glass formers has become a new glassy material. Borophosphate received a considerable attention because of their potential applications in optical technology. By combining glass forming units from borate and phosphate, the borophosphate glass will offer greater advantages because such glasses exhibit their different properties.

Furthermore, the borophosphate glass properties were effectively controlled by changing their composition. Thus, it facilitates the tailoring of the physical and chemical properties for specific technological application. In fact, the inclusion of borate into the phosphate glass network has been reported to increase the chemical durability of the phosphate glasses by contributing boron atoms into the system.
By increasing the chemical durability of this glass, it makes borophosphate glasses as one of the significant classes of glassy material because they can offer wider functional properties. The spectroscopic studies indicate that the glass system was improved by the incorporation of tetrahedral of boron and the desirable properties results also can be obtain (Chanshetti et al., 2011).

Borophosphate glasses offers variety of useful properties especially for optical applications due to their good optical properties such as low dispersion, good transparency and low refractive indices from the ultraviolet to the near-infrared regions. Borophosphate glasses are well known candidates for sealing applications such as low melting glass solder and glass to metal seal (Kesavulu et al., 2010). For example, zinc calcium doped borophosphate glasses are used as low-melting glass solders.

Besides that, the development of alkali and silver borophosphate glasses found their application as fast ion conductor (Gaafar et al., 2009). Previous study by Zheng et al., (2012) claimed that the forming properties of soda calcium phosphate glasses have been improved by addition of magnesium, potassium, strontium and boron. This new forming properties makes borophosphate glasses suitable for biomedical use and also for fiber drawing.

Furthermore, the presence of multi valence states of transition metal ions (TMI) in oxide glasses brings great interest because of their semiconducting properties. These additional properties are due to the electron hopping between two TMI with different valence states. By the definition, the elements that have partially filled d or f sub-shell in any common oxidation state are called transition elements. Even though this term usually refers to the d-block transition elements which include zinc as a member, zinc does not count as transition metal because it does not meet the definition.
In material science applications, zinc has attracted intensive research efforts because it has high refractive index, high thermal conductivity, antibacterial and UV-protection ability (Singh et al., 2009). ZnO has been used as additive in a variety of materials such as ceramic and glass. In concrete manufacturing, additional of ZnO can increase the resistance of concrete against water. Due to the increasing of global demands for green products, ZnO can be a suitable candidate for bio-application because zinc oxide is non-toxic and have less impact on the environment.

In the glass network, ZnO is a general glass modifier. It enters the glass network by breaking up the local symmetry of glass network. Thus, Zn\textsuperscript{2+} ions occupy the interstitial position and introduce the dangling bonds along NBO ions. Previous research on antimony borate glasses by Ghandi et al., (2009) reported the successful introduction of ZnO in the network with very high glass forming ability and high insulating character. Studing on zinc borophosphate glasses was report in few papers, regarding their applications as packaging and enameling solder glass, together with seals in flat panel displays (Koudelka et al., 2007).

The relation between structure and physical properties of glass consist of ZnO- \( \text{B}_2\text{O}_3\text{-P}_2\text{O}_5 \) within several composition have been studied and a model of evolution of glass structure from phosphate to borophosphate has been proposed. Previous studies have determined the preferences of BO\textsubscript{4} units at low \( \text{B}_2\text{O}_3 \) content and the presence of macroscopic phase separation at higher \( \text{B}_2\text{O}_3 \) content (Koudelka et al., 2001).

In industrial field, antimony oxide can be used as a flame retardant synergist in a substance, in order to reduce the speed of a chemical reaction in adhesives, plastics, rubber, fiberglass, textiles, and paper. The paint manufacturers use antimony oxide as a white pigment and sometimes used with other materials to form yellow pigments. It is also used as a fining agent or as degasser to removal of gases from fused glass in glass manufacturing. Besides, in order to turn a material opaque such as porcelain, antimony oxide was use as an opacifier in the enameling process. Glass
containing antimony being widely used as power limiters, optical switches and broad band optical amplifier operating around 1.5 μm in non linear optical devices.

Theoretically, antimony has a lone electron pair and involved in the glass in \(\text{SbO}_3\) structural units. Specifically, the antimony oxygen situated at three corners and lone pair of electrons of \(\text{Sb}^{3+}\) at the fourth corner localized in the third equatorial direction (Ghandi et al., 2009). \(\text{Sb}^{5+}\) ions also exist and participate in the formation of glass network with \(\text{Sb}^{5+}\text{O}_4\) structural units. Previous studies on antimony phosphate glass by Ghosh et al., (1998) showed that the hopping of electron between \(\text{Sb}^{3+}\) and \(\text{Sb}^{5+}\) caution makes the glass conduct electricity. He also stated that, the addition of antimony to \(\text{V}_2\text{O}_5\text{P}_2\text{O}_5\) glasses, improves the stability of the glass against moisture under ambient conditions.

Recent years, many researchers focused on non linear optical properties of borate and phosphate glass doped with various rare earth ions. There are few studies carried out about borophosphate glasses doped with rare earth ions. One of the primary spectral studies of rare earth oxide doped sodium borophosphate glass has been conducted and the result showed interesting features about the split band (Almeida et al., 2002). In fact, it only focused on ternary borophosphate system. Considering the advantages of borate glass and phosphate glass, it can be expected that rare earths ion doped borophosphate glasses would show excellent photoluminescence properties.

Spectroscopic instrument like infrared (IR), Raman and nuclear magnetic resonance (NMR) play important role in understanding the glass structure. These instruments give important information about the bonds and structural coordination in the glass system (Yano et al., 2003).
Infrared spectroscopy has been used to identify molecular vibration. Furthermore, the information about the band gap of the energy and structure of amorphous material can be determined by studying the optical absorption spectra of the glass (Meera, 1992). Besides that, transmission and absorption in the ultraviolet, infrared and visible regions can be used to study short-range of glass structures (ElBatal et al., 2012).

Luminescence glasses can be a good option to replace the conventional LED. This system does not need extra encapsulation because the glass itself can function as a protection layer for LED. The semiconductor chip and the normal plastic lens in current LEDs can be replaced to luminescence glass by reshaping the glass into a lens.

There are some advantageous when using luminescence glass as LED such as free from halo effect, simpler manufacture procedure, even can reduce the cost by having lower fabrication cost compare to phosphors LED (Zhu et al., 2007). In order to have a LED luminescence glass, an extensive research needs to be conducted. Rare earth ions in various glasses seem to be a great candidate because it can be easily fabricated in several forms (Kumar et al., 2010).

The luminescence glasses have important functions in the development of optoelectronic device and nonlinear optical material such as lasers and display material (Zhang et al., 2009; ElBatal et al., 2012). Other than that, transparent materials such as glasses doped with rare earth ion have shown their advantages in optical signal amplification for telecommunication (Lopez-Rivera et al., 2003).
1.2 **Statements of Problem**

 Previous studies on borophosphate glass stated that borophosphate glasses have acceptable chemical durability compared to pure borate and pure phosphate glasses (ElBatal et al., 2012). This glass can be a good network former because the large range of glass forming compositions (Kamitsos and Chryssikos, 1991). However, most of the researchers were more interested to study the structural and physical properties of this borophosphate glass system (Saranti et al., 2006; Lim et al., 2010). Unfortunately, only a few researchers carried out about borophosphate glasses doped with rare earth ions. There are limited studies on the luminescence properties of quaternary borophosphate system especially in the composition of antimony zinc borophosphate (ZnO-Sb2O3- B2O3-P2O5). In fact, they only focus on ternary borophosphate glass system. Therefore, this study was conducted to investigate the structural features of this glass system, as well as the effects of doping rare earth ions on its luminescence properties and the influence of rare earth ions to the structural features.

1.3 **Objectives of the Study**

 The objectives of this study are:

 i. To determine the most stable antimony zinc borophosphate glass composition.

 ii. To determine the infrared structural features of prepared undoped sample.

 iii. To determine the influence of rare earth ions to the structural features.

 iv. To choose the most suitable rare-earth ion for this glass composition.

 v. To find the optimum samarium concentration to get the best luminescence properties.
1.4  Scope of the Study

In order to achieve the objective of the study, the glasses sample based on different composition of antimony zinc borophosphate doped with various rare earths such as europium (Eu), erbium (Er), samarium (Sm) and neodymium (Nd) were prepared using melt quenching technique. The amorphous or crystalline phase was detected using X-Ray Diffraction (XRD) and the structural features of the glasses were investigated using Infrared Spectroscopy (IR). The luminescence properties of the samples were measured using photoluminescence spectroscopy (PL).

1.5  Significant of the Study

This study is conducted to find out the modification on borophosphate glass network by antimony trioxide (Sb$_2$O$_3$) and zinc oxide (ZnO). Due to the limited study based on P$_2$O$_5$-B$_2$O$_3$-Sb$_2$O$_3$-ZnO glass; this present study has been proceed for further understanding and information about the structural features of the glass. The study of the zinc and antimony effect in borophosphate glasses is important to determine the stability of the glass network structure. The influenced of Eu, Er, Sm and Nd on the structural features act as additional information to further study on this field. By adding suitable rare earth ions into the Sb$_2$O$_3$ - ZnO based borophosphate glass system; new luminescence materials can be developed because these materials emit light in the visible range. Furthermore, the relationship between the dopand concentrations with the luminescence properties also needs to be understood. At the end, this material is a potential luminescence material.
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