STRUCTURAL AND LUMINESCENCE PROPERTIES OF ANTIMONY, LEAD, BISMUTH ZINC BOROPHOSPHATE GLASSES DOPED IRON AND TITANIUM

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To my beloved family and friends

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ABSTRACT

Three series of antimony (Sb), lead (Pb) and bismuth (Bi) zinc borophosphate glass were prepared at composition $x$$Sb_2O_3$-(50-$x$)$P_2O_5$-20ZnO-30$B_2O_3$:2$Fe_2O_3$, xPbO-(50-x)ZnO-10B_2O_3-40P_2O_5 and $x$$B_2O_3$-(60-$x$)$P_2O_5-10Bi_2O_3$-30ZnO with $0 \leq x \leq 50$ mol%. All glasses were successfully fabricated by melt quenching method. The X-Ray Diffraction (XRD) confirmed the amorphous nature of glass samples. The Energy Dispersive X-Ray (EDX) was used for elemental analysis in the sample. The EDX spectrum showed the existence of antimony, lead, bismuth and zinc in glass samples. The structural vibrations were measured by the Fourier Transform Infrared (FTIR) spectroscopy. The analysis indicated the borophosphate glass system is dominated by the linkages of P-O, B-O-B, P-O-P, while the recorded stretching bond by the linkages of B-O, PO_2, BO_3 and BO_4. The glasses were doped by the iron (Fe) and titanium (Ti) for luminescence study. The Photoluminescence (PL) spectra showed the Fe emission at 402 nm, 464 nm and 540 nm are not affected by composition variation in antimony zinc borophosphate system. The Fe showed the same emission as the Fe was doped in lead zinc borophosphate glass. However, the 540 nm emission diminished when Fe was doped in bismuth zinc borophosphate glass. The Ultraviolet-Visible (UV-Vis) absorption spectra showed that the Fe absorbed at wavelength 277 nm to 430 nm as it doped to antimony zinc borophosphate system. As the Sb content increased up to 20 mol%, the absorption range extended to 462 nm. Fe doped lead zinc borophosphate glass was only absorbed at wavelength 200 nm to 385 nm. This range is reduced to 350 nm when Fe doped to bismuth zinc borophosphate glass. Ti doped lead zinc borophosphate glass absorbed at 200 nm to 335 nm while only absorbed at 200 nm to 314 nm when Ti was doped to bismuth zinc borophosphate glass.

ABSTRAK

Tiga siri kaca antimoni (Sb), plumbum (Pb) dan bismut (Bi) zink borofosfat telah disediakan dalam komposisi xSb$_2$O$_3$-(50-x)P$_2$O$_5$-20ZnO-30B$_2$O$_3$:2Fe$_2$O$_3$, xPbO-(50-x)ZnO-10B$_2$O$_3$-40P$_2$O$_5$ dan xB$_2$O$_3$-(60-x)P$_2$O$_5$-10Bi$_2$O$_3$-30ZnO dengan $0\leq x \leq 50$ mol%. Semua kaca telah berjaya dihasilkan dengan menggunakan teknik sepuh lindap. Belauan Sinar-X (XRD) mengesahkan sifat amorfus sampel kaca. Serakan Tenaga Sinar-X (EDX) telah digunakan untuk menganalisa unsur dalam sampel. Spektrum EDX menunjukkan kewujudan antimoni, plumbum, bismut dan zink dalam sampel kaca. Getaran struktur telah diukurkan dengan Inframerah Transformasi Fourier (FT-IR). Analisa menunjukkan sistem kaca borofosfat didominasi oleh rangkaian P-O, B-O-B, P-O-P manakala peragangan ikatan merekodkan raingkaian B-O, PO_2, BO_3 and BO_4. Sampel kaca telah didopkan dengan besi (Fe) dan titanium (Ti) untuk kajian luminasi. Spektrum fotoluminasi menunjukkan pancaran Fe pada 402 nm, 464 nm dan 540 nm tidak terubah terhadap variasi komposisi kaca antimoni zinc borofosfat. Fe juga menunjukkan pancaran yang sama walaupun didopkan dalam kaca plumbum zink borofosfat. Namun, pancaran pada 540 nm telah lenyap semasa Fe didopkan dalam kaca bismut zink borofosfat. Spektrum penyerapan lembayung (UV-Vis) menunjukkan Fe menyerapkan panjang gelombang dari 277 nm hingga 430 nm bila ia didopkan kepada kaca antimoni zink borofosfat. Apabila kandungan Sb meningkat sehingga 20 mol%, julat penyerapan telah meningkat sehingga 462 nm. Kaca Fe mengedop plumbum zink borofosfat menyerap panjang gelombang dari 200 nm sehingga 385 nm. Julat ini telah menyusut sehingga 350 nm apabila Fe mengedop dalam kaca bismut zink borofosfat. Kaca Ti mengedop plumbum zink borofosfat menyerap pada panjang gelombang 200 nm hingga 335 nm manakala ia hanya menyerap pada 200 nm hingga 335 nm apabila Ti mengedopkan pada kaca bismut zink borofosfat.

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LIST OF SYMBOLS

°C	-	Degree celsius
d	-	Spacing between parallel plannes
θ	-	Angle
λ	-	Wavelength
e^-	-	Electron
I_t	-	Intensity of light pass through sample
I_0	-	Intensity of light source
~	-	Around
%	-	Percent
ν_s	-	Symmetric stretching
g	-	Gram
cm	-	Centimeter
nm	-	Nanometer

LIST OF ABBREVIATIONS

EDX	-	Energy Dispersive X-ray
FT-IR	-	Fourier Transform Infrared
IR	-	Infrared
NMR	-	Nuclear Magnetic Resonance
PL	-	Photoluminescence
SEM	-	Scanning electron microscope
UV	-	Ultraviolet
Vis	-	Visible
XRD	-	X-ray Diffraction
Al_2O_3	-	Aluminium oxide
B_2O_3	-	Boron trioxide (Borate)
Bi_2O_3	-	Bismuth (III) oxide
Fe_2O_3	-	Iron (III) oxide
Gd_2O_3	-	Gadolinium (III) oxide
H_3BO_3	-	Boric acid
H_3PO_4	-	Phosphoric acid

KBr	-	Potassium bromide
MnO_2	-	Manganese dioxide
Nd_2O_3	-	Neodymium (III) oxide
P_2O_5	-	Phosphorus pentaoxide (Phosphate)
Pb_3O_4	-	Lead (IV) oxide
Sb_2O_3	-	Antimony trioxide
SiO_2	-	Silicon dioxide
TiO_2	-	Titanium dioxide
Y_2O_3	-	Yttrium oxide
B	-	Boron
Ba	-	Barium
Bi	-	Bismuth
Ca	-	Calcium
Cu	-	Copper
Cr	-	Chromium
Cs	-	Cesium
Dy	-	Dysprosium
Eu	-	Europium
Fe	-	Ferum/Iron
Gd	-	Gadolinium

H	-	Hydrogen
K	-	Potassium
La	-	Lanthanum
Li	-	Lithium
Mg	-	Magnesium
Mn	-	Manganese
Na	-	Sodium
O	-	Oxide
P	-	Phosphorus
Pb	-	Lead
Rb	-	Rubidium
Si	-	Silicon
Sm	-	Samarium
Sn	-	Tin
Ti	-	Titanium
V	-	Vanadium
Zn	-	Zinc
Q^3	-	Tetrahedral (vitreous v-P_2O_5)
Q^2	-	Metaphosphate
Q^1	-	Pyrophosphate

Q^0	-	Orthophosphate
NBO	-	Non bridging oxygen
MCA	-	Multi channel analyzer

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Chapter 1

Introduction

1.0 Introduction

This chapter is about the study background, problem statement, objective of study, scope of study and significance of study. We'll discuss on what had been done by other researchers and the problem in their studies. Besides, we will point out why we want to carry out this study.

1.1 Study Background

Glass is defined as an inorganic product of fusion which has been cooled into rigid condition without crystallization. By this definition, a glass is a non-crystalline materials which can be obtained by various methods such as melt quenching, chemical vapour deposition, sol-gel process, etc (Yamane *et al*, 2000). Glass was also known as amorphous solid. It can be formed by 'glass forming substances' such as SiO_2, B_2O_3, P_2O_5 with 'modifier' metal oxide (Scagliotti *et al*, 1986). The addition of modifier into glass network could alter glass properties and durability towards atmosphere. In terms of atomic arrangement, glass has random atomic arrangement unlike crystal with well atomic arrangement. Glass can be used for building and car's windows, containers, decoration and other else. In recent technology application, it has being used for television display panel, lighting, optical lenses, fiber optic and so on.

Borate, B_2O_3 was a well known host in glass research area. Borate glass consists of trigonal BO_3 and tetrahedral BO_4 structure units. Borate glass can be easily melted, having smaller mass compare to other glass network former, chemically durable and thermally stable. Besides, it has high transparency which suitable for optical materials. Moreover, it acted as a good host for transition metal ions (El Batal *et al*, 2008). However, borate glass has limited efficiency for infrared and upconversion visible emission due to its high phonon energy. There was also a special phenomena occurring in borate glass, called 'boron anomaly', where BO_3 transformed to BO_4 units. The researcher explained it as appearance of BO_4 structure due to addition of alkali oxide up to 20 mol% into borate system (Khalifa *et al*, 1991). Khalifa *et al* implemented Fourier Transform Infrared (FT-IR) to study structural units of sodium, lithium, potassium borate glass. From the FT-IR result, they interpret peaks at 1350 cm^{-1} as BO_3 transformation into BO_4 units. Their study also revealed the increasing alkali oxide content slightly shifted the absorption band of FT-IR spectra to longer wavelength due to the decreases of ligand field strength. Recent year, researchers started to use heavy metal oxide to modify borate glass. Heavy metal oxide offered a wide range of glass formation composition. In bismuth borate glass, as Bi_2O_3 content increased, the glass molar volume increased while the glass transition temperature decreased (Bajaj *et al*, 2009). Besides, the heavy metal borate glass is able to shield the gamma radiation. Interaction of gamma ray upon bismuth borate glass had been studied by Ultraviolet Visible (UV-Vis) and FT-IR (El Batal *et al*, 2007). Their results showed no obvious change for UV-Vis spectra upon gamma radiation. FT-IR spectra interpretation suggested introduction of Bi_2O_3 may transform BO_3 to BO_4. A recent study on lead borate glass with gamma radiation interaction was done as well. This system measured by UV-Vis and FT-IR (El Batal, 2012). Both of the measurement results showed no obvious changes for irradiated samples compare to un-radiated samples. Furthermore, FT-IR displayed the presence of BO_3, BO_4 and Pb-O units. So, heavy metal borate glass is able to act as gamma ray shielding and this ability was confirmed by the researchers.

Another glass network former was phosphate, P_2O_5. Phosphate glass was analyzed as basic structure PO_4 tetrahedral connected through bridging oxygen. Generally, it was described as Q^n terminology with n as number of bridging oxygen per tetrahedron. This structure categorized as Q^3 tetrahedral (vitreous v-P_2O_5), Q^2 (metaphosphate), Q^1 (pyrophosphate) and Q^0 (orthophosphate) (Hussin *et al*, 2009). Phosphate glass has low viscosity, high refractive index, high thermal expansion coefficient and UV transparency (Majjane *et al*, 2014). However, the exploration on phosphate glass become slow and limit due to its poor chemical durability. Recently, calcium phosphate glass applied as bones and dental implants due its biocompatible properties. It is also used as solid state laser and glass-to-metal seal (Majjane *et al*, 2014; Fu and Mauro, 2013). The introduction of heavy metal oxide such as PbO, Al_2O_3 into phosphate glass system increases the glass resistant toward moisture, higher chemical durability and enhance the mechanical strength (Rao *et al*, 2012). A study on heavy metal oxide Sb_2O_3 replaced ZnO in ZnO-Sb_2O_3-P_2O_5 glass system concluded that the Sb_2O_3 improve the glass chemical durability as phosphate chain was replaced by P-O-Sb bonds (Zhang *et al*, 2008). Another study measured lead phosphate glass by X-ray Diffraction (XRD) and FT-IR. XRD had confirmed that the glass system was amorphous. In FT-IR measurement, the lead phosphate glass exhibited the Pb-O stretching vibration, deformation modes of the P-O glass network, stretching modes of non-bridging P-O bonds, asymmetric stretching vibration of PO^{2-}, asymmetric and symmetric stretching mode of the P-O-P bonds (Pisarska *et al*, 2011). Ternary zinc bismuth phosphate was also studied. FT-IR revealed almost the same phosphate bonding vibration as in lead bismuth system. The author suggested bismuth had depolymerised phosphate chain with formation of P-O-Bi unit and the incorporation of Bi as BiO_6 octahedral in the glass matrix. Other features were the glass density and glass transition temperature increase with the increase of Bi_2O_3 content. (Im *et al*, 2010). The introduction of heavy metal oxide into phosphate glass improved the glass moisture resistant and enriched information in phosphate glass research field.

Recently, researchers started to combine both borate and phosphate to make a new glass system, called borophosphate glass. Borophosphate glass provides better chemical durability compare to pure borate and pure phosphate glass system while maintaining the low melting point. It was expected to have distinctive properties from pure B_2O_3 and pure P_2O_5 network. As result, the structural of borophosphate glass shows the combination of PO_4, BO_3, BO_4 units. Borophosphate glass is transparent from ultraviolet to near infrared region. Moreover, borophosphate provided the other application as solder glasses, fast ionic conductors and recently shown up for biomedical application (Abdelghany *et al*, 2012). There was some research study on borophosphate glass modified with heavy metal oxide. The lead borophosphate glass was studied using Raman Spectroscopy (Koudelka *et al*, 2003). From the result of Raman spectroscopy, lead borophosphate glass demonstrated the stretching vibrations of O-P-O bonds, symmetric stretching frequency of $\nu_s(PO_2)$, vibrations of P-O bonds and stretching vibrations of oxygen atoms in P-O-P units. Tin (Sn) borophosphate glass was also investigated by Raman Spectroscopy. It has reported the stretching vibration of P-O, symmetric stretching mode of bridging oxygens which link the phosphate tetrahedral and bonding of Sn-Borate (Lim *et al*, 2010).

The luminescence is a phenomenon where the substance emits light under the influence of certain radiation. It might be cause by chemical reaction, electrical energy, subatomic motion and can be measured by Photoluminescence (PL) Spectroscopy. To make a luminous substance, a doping process is needed. Doping is a process where small amount of impurity was added into substance to alter its properties. This impurity is also known as dopant or so called activator. The rare earth elements are well known dopant for the glass research due to its visible light emission characteristic. Europium (Eu) is a frequent used dopant as it is emitted at red colour region. In number of glass research, Eu has doped the zinc borate glass, aluminium phosphate glass and zinc borophosphate glass. The studies reveal that Eu is consistently emitted at wavelength ~592 nm and ~613 nm although the host network were different (Elisa *et al*, 2013; Ivankov *et al*, 2006; Lian *et al*, 2007). Dysprosium (Dy) is also frequently use for doping process. Dy doped the lead borate glass, lead phosphate glass and also sodium lead borophosphate glass. As the result, Dy emitted at ~480 nm and ~573 nm even with different host network (Kiran and Kumar, 2013; Pisarska, 2009; Pisarski *et al*, 2014). On the other hand, the transition metal element also had been used as dopant. Among all, manganese (Mn) became a popular dopant for glass luminescence research. Manganese doped borogermanate glass possessed a strong peak at 623 nm (Sun *et al*, 2013). However, as Mn doped the sodium lead borophosphate glass, it does emitted at 560 nm (Kiran *et al*, 2011a).

In calcium zinc borophosphate glass, researcher varies Mn concentration from 2-10 mol%. It does shown the emission band shifted from 582 nm to 650 nm with the increase of Mn concentration (Wan *et al*, 2014).

In this study, we will investigate the zinc borophosphate glass modified with 3 different heavy metal elements: antimony, bismuth and lead. The glass sample from these 3 types of glass system will be doped with transition metal iron (Fe) and titanium (Ti).

1.2 Statement of Problem

In this study, we will investigate antimony, bismuth, lead modified zinc borophosphate glass. Although there were some structural studies done on antimony zinc borophosphate glass and lead zinc borophosphate glass, but these studies focused to Raman and Nuclear Magnetic Resonance (NMR) Spectroscopy measurements only. Furthermore, there was no investigation reported on bismuth zinc borophosphate glass. To enrich the structural information on heavy metal oxide modified zinc borophopshate glass, we will study the glass system by using XRD, FT-IR and Energy Dispersive X-Ray (EDX) Spectroscopy. Besides, there was no study on luminescence properties of these glass systems. We will dope the glasses with transition metal ions and examine it by PL and UV-Vis Spectroscopy.

1.3 Objectives of Study

- To determine structural properties of antimony zinc borophosphate glasses on variation of antimony and phosphate content
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- To determine structural properties of lead zinc borophospahte glasses on variation of lead and zinc content

- To determine structural properties of bismuth zinc borophosphate glasses on variation of borate and phosphate content
- To determine the luminescence properties of antimony, bismuth, lead modified zinc borophosphate glass doped with iron and titanium.

1.4 Scope of Study

The structural properties of glass system will be measured by XRD, FT-IR and EDX Spectroscopy. XRD is used to examine the amorphous nature of glass to confirm the glass samples were not crystalline. For FT-IR study, it is used to reveal structure bonding between borate and phosphate unit of glass. On the other hand, EDX Spectroscopy is responsible to detect the existence of modifier element in the sample and to ensure it does not sublimated in the sample's fabrication process.

Meanwhile, luminescence properties of glass system are characterized by PL and UV-Vis Spectroscopy. By PL spectroscopy, the excitation and emission profile of dopant will be discovered to study its luminescence properties. Finally, UV-Vis spectroscopy will be recorded the absorption range of dopant in each sample.

1.5 Significance of Study

This study is important to provide more information on glass research field especially borophosphate glass research. The structural information on heavy metal oxide zinc borophosphate glass will be improved. Besides, the luminescence properties of this glass system will be revealed.

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