STRUCTURAL AND LUMINESCENCE PROPERTIES OF MAGNESIUM ALUMINATE BORATE GLASS DOPED WITH Eu AND Dy IONS

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To my beloved mother and father

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ABSTRACT

A series of glasses based on xMgO-(95–x)B_2O_3-5Al_2O_3 where 15≤ x ≤25 mol% and xMgO-(90–x)B_2O_3-10Al_2O_3 where 10≤ x ≤30 mol% have been prepared using melt quenching technique. The amorphous phases were identified using X-ray diffraction (XRD) and the mode of vibrations for these glasses has been determined by means of Fourier Transforms infrared (FTIR) spectroscopy. The results of XRD patterns indicate that the glasses are amorphous phase. FTIR measurements revealed that the network structure of the studied glasses is mainly based on BO_3 and BO_4 units placed in different structural groups which the BO_3 units being dominant. The introduction of low Al_2O_3 content caused the conversion of BO_3 units into BO_4 units. Meanwhile when Al_2O_3 content is increase to 10 mol%, the conversion from BO_4 to BO_3 occurs. This phenomenon is usually observed in borate glass which is called "boron anomaly". In order to obtain the luminescence properties, these glasses were doped with 1 mol% Dy^{3+} and Eu^{3+} ions each in composition of 30MgO-10Al_2O_3-60B_2O_3 and 20MgO-10Al_2O_3-70B_2O_3. The absorption spectra obtained from UV-Visible spectrometer of the glasses sample show that there were obvious absorptions peaks in infrared region for both Dy^{3+} and Eu^{3+} ions. Photoluminescence spectra for both ions were emitted in visible region. The Dy^{3+} emission is due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition (blue region) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition (yellow region). Meanwhile the red emission spectra are due to transition of $^5D_0 \rightarrow {}^7F_2$ in Eu^{3+} ion. In addition, in this study revealed that Dy^{3+} ion dependent on host composition whereas Eu^{3+} ion is not dependent on host composition.

ABSTRAK

Sampel kaca berdasarkan siri sistem xMgO:(95–x)B_2O_3:5Al_2O_3 dengan 15≤x≤25 mol% dan sistem xMgO:(90–x)B_2O_3:10Al_2O_3 dengan 10≤ x ≤30 mol% telah disediakan berdasarkan teknik sepuh lindap. Fasa hablur kaca dikenalpasti menggunakan pembelauan sinar-x (XRD) dan mod getaran kaca telah ditentukan menggunakan teknik spektroskopi inframerah (FTIR). Hasil yang diperoleh daripada XRD telah menunjukkan sample kaca adalah amorfos. Pengukuran struktur menggunakan teknik FTIR telah menunjukkan bahawa kumpulan berfungsi sampel kaca terdiri daripada unit-unit BO_3 dan BO_4 yang terletak pada kumpulan yang berlainan dimana unit BO_3 adalah dominan. Pengenalan bahan Al_2O_3 telah menyebabkan unit BO_3 bertukar kepada unit BO_4. Manakala penambahan komposisi Al_2O_3 kepada 10 mol% telah menyebabkan penukaran unit dari BO_4 kepada BO_3. Fenomena ini seringkali dijumpai dalam kaca borat, dipanggil "anomali boron". Untuk mendapatkan sifat luminesens, kaca-kaca ini akan didop dengan ion Dy^{3+} dan Eu^{3+} sebanyak 1 mol% setiap satunya pada komposisi 30MgO:10Al_2O_3:60B_2O_3 dan 20MgO:10Al_2O_3:70B_2O_3. Spektrum penyerapan yang diperoleh daripada kaca ini menunjukkan terdapat puncak serapan yang jelas pada julat inframerah untuk kedua-dua ion Dy^{3+} dan Eu^{3+}. Spektra fotoluminesens untuk kedua-dua ion telah dipancarkan pada julat cahaya nampak. Pancaran Dy^{3+} adalah disebabkan oleh transisi $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (julat kawasan biru) dan transisi $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (julat kawasan kuning). Manakala pancaran merah adalah disebabkan oleh transisi $^5D_0 \rightarrow {}^7F_2$ daripada ion Eu^{3+}. Selain itu, ion Dy^{3+} bergantung kepada hos manakala ion Eu^{3+} tidak bergantung kepada komposisi hos.

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λ	Wavenumber
n	The refractive index of the medium
d	Distance between atomic layers in a crystal
θ	Angle
υ	Vibration frequency
k	Force constant
μ	Reduced mass
m_1 and m_2	Masses of atom 1 and 2

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Glass material is not new. It has been used since 4000 years ago by man during ancient Egypt. The interesting facts about the glass are it acquires many unique properties such as it is clear, transparent and not corrode. Glass is commonly used for windows, bottles and lamp bulb.

Some oxides, called glass former, have the ability to form glasses by themselves or by mixing with other network formers. Examples of the oxides are SiO_2, P_2O_5 and B_2O_3. They are capable of forming a 3D network with oxygen which will provide strong covalent bond. The glass is formed by heating the oxides up to the glass melting temperature and quickly cooled to ensure the glass will not crystallize. That is why the glass is also called “supercooled liquid”.

There are many techniques can be used in order to prepare a glass sample. The most conventional way is by the melt quenching technique. Nevertheless due to the research in glass, many techniques of glass preparation had been used. One of the most popular techniques nowadays is the sol-gel method because it deals with low temperature preparation and homogenized composition compared to the conventional method. However, the method of preparation is quite complex, time consuming and most of the material that can be used is very expensive.

Borate glass recently has been the subject of intensive investigations because of their technological and scientific importance. It offers promising choice especially for thermoluminescence applications due to its high sensitivity, low cost and easy preparation (Jiang L.H. *et al.*, 2009). In terms of luminescence, rare earth doped borate has more attention because it has high luminescence, great color coordinate and low thermal degradation (Wang F. *et al.*, 2008).

Unfortunately borate glasses alone are not a stable compound even though it is well known as the glass former. It can easily crystallize after melting and it has hygroscopic properties which often limit their practical uses. So, in order to reduce these problems and enhance the properties of the glass, another oxide must be added to the system such as metal oxides or alkali oxides. Some examples of these modifiers are magnesium oxide, sodium oxide or strontium oxide. It can act as a network former and it have the ability to change the structural features of the borate glass (Hussin R. *et al.*, 2009).

In addition, aluminate borate glasses containing alkali earth oxides is interesting to study because of their unique properties such as high hardness, high chemical resistance, excellent chemical durability and low melting temperature compared to the commercial silicate based glasses (El-Moneim A.A. *et al.*, 2006). Besides that, addition of aluminium oxide in borate glass modifies the network's structural units causing a change of boron coordination from BO_3 to BO_4 units. The glass-forming regions in these systems can also be extended by introducing Al_2O_3 (Dominiak-Dzik G. *et al.*, 2006).

Unfortunately, the study of ternary magnesium aluminate borate glass is very few. Raju G.N. *et al.* (2009) has studied this ternary glass system to determine the spectroscopic and dielectric properties of the system. Meanwhile Hamzawy E.M.A. *et al.* (2008) only studied the vitrification and devitrification phenomena in the ternary system. Nevertheless, studying this ternary system is very significant because they are very stable against devitrification, posses high strength, toughness and have very low thermal expansion (Raju G.N. *et al.*, 2009).

Alkaline earth glass doped with rare earth (RE) ions has attracted research interests in the field of photoluminescence since they are suitable hosts with high chemical stability, offers better homogeneity and lowers sintering temperature. Rare-earth doped glasses are important materials for optical applications such as lasers, sensors and optical amplifiers. Trivalent rare earth ions such as Er^{3+}- and Tm^{3+}-doped phosphate, silicate, germanate and tellurite glasses have been developed for infrared active optical devices. Recently, research focus on rare earth doped glasses is not limited to infrared optical devices but there is a growing interest in visible optical devices. With the increasing demand on various visible lasers and light sources, further investigations in other rare-earth ions, such as Dy^{3+}, Sm^{3+} and Eu^{3+} ions, are becoming more significant (Azeem P.A. *et al.*, 2009)

The trivalent europium ion, Eu^{3+} is the mostly used choice to optically activate glass matrices is due to the fact that Eu^{3+} ($4f^6$) ions emit narrow-band, almost monochromatic light and have long life time of the optically active states. Eu^{3+}- doped phosphors are commonly used as red emitting materials for field emission technology and LEDs, which exhibit higher luminescence efficiency compared with other luminous materials. Further, Eu^{3+} ions have often been used as probes for estimation of local environment around the Ln^{3+} ions in different matrices. This is because useful information about the local structure around Eu^{3+} ions can be obtained quite easily from its *f–f* transition spectra. Since the ground $^7F_0$ state and the first excited $^5D_0$ state of Eu^{3+} ions are non-degenerate under any symmetry, information regarding the local environment around the Eu^{3+} ion depends only on the splitting of the $^5D_0 \rightarrow ^7F_J$ emission spectra.

Meanwhile, luminescence materials doped with Dy^{3+} have drawn much interest because of its white emission. Dysprosium-doped solid-state systems can be quite easy excited by the commercial UV or blue LEDs, because their excitation spectra exhibit several 4f-4f electronic bands located in the 340-480 nm spectral range. The luminescence spectrum of Dy^{3+} consists of two relatively intense bands in the visible spectral region that correspond to the $^4F_{9/2}$ - $^6H_{15/2}$ (blue) and $^4F_{9/2}$ - $^6H_{13/2}$ (yellow) transitions, respectively (Pisarska J. *et al.*, 2010). Dy^{3+} is known as a good activator because the two dominated band in the emission spectra and its position depends strongly on the crystal field of the lattice used. Hence, luminescence materials doped with Dy^{3+} can produce white emission by adjusting the yellow to blue intensity ratio value, which can be used as potential white phosphors (Hussin R. *et al.*, 2009).

1.2 Problem Statement

The binary borate system has been study by many researchers. Unfortunately, there is lacking of study on the ternary borate system especially in the composition of magnesium aluminate borate. Few studies had been done in this system but are limited to certain properties and doping with rare earth ions is not study. Therefore, the present study is done in order to know the structural features of the doping and undoped glasses besides the effect of doping rare earth ion on luminescence properties and host composition.

1.3 Objectives

The objectives of this study are:

a) To prepare the glass based on composition of magnesium aluminate borate system doped and undoped.
b) To determine the mode of vibrations of the doped and undoped
c) To determine the absorption properties of the doped samples.
d) To determine the luminescence properties of the doped and undoped samples.

1.4 Scope of Study

In order to achieve the objectives, the study has been divided into several scopes which are:

a) Preparation of undoped MgO-Al_2O_3-B_2O_3 and doped with Eu^{3+} and Dy^{3+} ions using melt quenching technique.
b) Determination of the amorphous phase of the obtained glass using X-ray diffraction.
c) Determination of the vibrations mode of the prepared sample using FTIR Spectroscopy.
d) Determination of the absorption properties of the samples using UV-Vis Spectroscopy.
e) Determination of the emission and excitation spectra of the doped glasses using Photoluminescence Spectroscopy.

1.5 Glass System Chosen

In order to achieve the aims of these studies, two series of glass samples has been prepared based on constant aluminum with variation of magnesium oxide. Series I is based on composition of xMgO:(95–x)B_2O_3:5Al_2O_3, with 15≤ x ≤25, meanwhile, series II is based on composition of xMgO:(90–x)B_2O_3:10Al_2O_3, with 10≤ x ≤30. Four sample of glass based from series II has been prepared doped with 1 mol % each with Eu_2O_3 and Dy_2O_3.

1.6. Significant of the study

Due to the limited of study based on MgO-Al_2O_3-B_2O_3 glass, this present study has been done to understand further the structural features of the glass. By adding doping to the system, new materials can be developed as new luminescence materials. These materials can emit light at the visible range and can be used as a long after glow material. Furthermore, the relationship between the hosts with the luminescence properties can also be understood. At the end, this material is potential as thermoluminescence sensor.