THE STRUCTURAL AND LUMINESCENCE PROPERTIES OF DIVALENT EUROPIUM ION-DOPED BARIUM BOROPHOSPHATE

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To my beloved father and mother,
Mr. Mustapa Kamal Bin Mohd Tahir and Rokiah Binti Idrus,
my siblings, friends and special appreciation to my supervisor,
Dr. Mohd Nor Md Yusuf

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ABSTRACT

A series of $BaBPO_5$ phosphor samples doped with different concentration of Eu^{2+} ions, up to 0.6 mol % were synthesized by solid state reaction method. The mixtures of $(NH_4)_2HPO_4$, $BaCO_3$, H_3BO_3 and Eu_2O_3were heated in pure argon atmosphere at 850°C where the reduction of Eu^{3+} to Eu^{2+} ions occurred. The structural properties of the phosphors were analyzed by X-ray diffraction technique (XRD) and Fourier transform infrared spectroscopy (FTIR). The morphology of the phosphors was investigated by scanning electron microscope (SEM). The luminescence properties of the phosphors were observed at room temperature using photoluminescence (PL) spectrometer where the effects of Eu^{2+} ions in the phosphors were investigated. The XRD results show that, all the doped and undoped samples are polycrystalline with hexagonal host structure. The SEM images of the samples show particles of $BaBPO_5$ were agglomerated with irregular morphology and no significant difference were found between the doped and the undoped samples. The particles have an average size of about 0.1 – 1 μm. The similarity in the morphology suggests that the Eu^{2+} ions do not cause any changes to the host structure. The PL results show that the undoped sample does not have distinct luminescence characteristic while the samples doped with Eu^{2+} ions have broad emission band in violet region of 350 – 420 nm centered at 383 nm which is attributable to transition of configuration state $4f^6\ 5d^1 \rightarrow 4f^7$ of the Eu^{2+} ions. The emission intensity is affected by the concentration of Eu^{2+} where optimum intensity was observed for 0.2 mol % of Eu^{2+} ions. The FTIR spectra show that the samples are dominated by tetrahedral group of BO_4 and PO_4 to form a 3-dimensional network. The occurrence of emission lines in violet region indicates that this phosphor has potential for application in solid-state lighting.

ABSTRAK

Satu siri sampel fosfor $BaBPO_5$ didopkan dengan ion Eu^{2+} yang berbeza kepekatan sehingga 0.6 mol % telah disintesis dengan kaedah tindak balas keadaan pepejal. Campuran bahan $(NH_4)_2HPO_4$, $BaCO_3$, H_3BO_3 dan Eu_2O_3 dipanaskan dalam persekitaran atmosfera argon tulen pada suhu 850°C di mana penurunan ion Eu^{3+} kepada ion Eu^{2+} berlaku. Ciri struktur sampel fosfor dianalisis dengan menggunakan teknik pembelauan sinar-X (XRD) dan spektroskopi inframerah transformasi Fourier (FTIR). Morfologi fosfor dikaji dengan menggunakan mikroskop pengimbas elektron (SEM). Sifat luminisen fosfor dicerap pada suhu bilik dengan menggunakan spektrometer fotoluminisen (PL) di mana kesan ion Eu^{2+} dalam bahan fosfor telah dikaji. Keputusan XRD menunjukkan kesemua sampel sama ada didop atau tanpa dop adalah polihablur dengan struktur perumah heksagon. Imej SEM sampel menunjukkan zarah $BaBPO_5$ bergumpal dengan struktur morfologi yang tidak teratur dan tiada perbezaan yang ketara antara sampel yang didop dan tanpa didop. Zarah mempunyai saiz purata sekitar 0.1 – 1 μm. Sifat morfologi yang hampir sama menunjukkan ion Eu^{2+} tidak menyebabkan perubahan kepada struktur perumah. Keputusan analisis PL menunjukkan sampel tanpa dop tiada sifat luminisen yang berbeza manakala sampel yang didop dengan ion Eu^{2+} mempunyai jalur pancaran yang lebar pada kawasan ungu dengan panjang gelombang 350 – 420 nm dan berpusat pada 383 nm yang berpunca daripada peralihan konfigurasi aras $4f^6\ 5d^1 \rightarrow 4f^7$ ion Eu^{2+}. Keamatan pancaran dipengaruhi oleh kepekatan ion Eu^{2+} dengan keamatan optimum dicerap bagi sampel 0.2 mol % ion Eu^{2+}. Spektrum FTIR menunjukkan sampel didominasi oleh kumpulan tetrahedron BO_4 dan PO_4 untuk membentuk rangkaian 3-dimensi. Kejadian garisan pancaran di kawasan ungu menunjukkan bahan fosfor ini berpotensi dalam aplikasi pencahayaan keadaan pepejal.

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LIST OF ABBREVIATION

Ba	Barium
$BaCO_3$	Barium carbonate
$BaBPO_5$	Barium borophosphate
$BaBPO_5$: Eu^{2+}	Barium borophosphate doped europium ion
Ca	Calcium
$CaCO_3$	Calcium carbonate
CO	Carbon oxide gases
CRT	Cathode ray tube
Eu	Europium
Eu_2O_3	Europium oxide
FT-IR	Fourier transform infrared
H_2	Hydrogen gases
H_3BO_3	Boric acid
LED	Light emitting diode
LCD	Liquid crystal device
Mg	Magnesium
$MgCO_3$	Magnesium carbonate
N_2	Nitrogen gases
NBO	Non-bridging oxygens
$(NH_4)_2HPO_4$	Di-ammonium hydrogen phosphate
OLED	Organic light-emitting diode
PDP	Plasma display panel
PL	Photoluminescence
RE	Rare earth
S	Sample

SEM	Scanning electron microscopy
Sr	Strontium
SrO_3	Strontium carbonate
XRD	X-ray diffraction

LIST OF SYMBOLS

Å	Angstroms = 10^{10}
c	Speed of light = 3×10^8 ms^{-1}
d	Distance between crystal planes
E	Energy
h	Plank's constant = 6.626×10^{-34} m^2 kg s^{-1}
J	Joule
k	Force constant of the bond (Nm^{-1})
m_1	relative atomic mass of M_1
n	Integer number (an order of reflection)
N	Newton
R_c	Critical transfer distance
u	atomic mass unit = 1.66×10^{-27} kg.
V	Unit cell volume ($Åm^3$)
x_c	Critical concentration of activator
Z	Number of formula units per unit cell
θ	Diffraction angle (grazing angle)
λ	Wavelength
ν	Frequency (Hz)
$\overline{\nu}$	Wavenumber (cm^{-1})
ν_1	symmetric stretching modes
ν_3	asymmetric stretching modes
δ	bending mode

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Today, phosphor-based devices such as fluorescent lamp and light emitting diode (LED) lamp are widely used almost in all buildings in the world. Likewise, phosphor-based luminescent materials are widely used in technological areas such as cathode ray tube (CRT), plasma display panel (PDP) and phosphorescent paint (Yonesaki and Matsuda, 2011; Lakshmanan, 2008).

Luminescence in solid is a phenomenon in which electronic states of the solid are excited by an external source and this excitation energy is released as light which includes the visible, the near-ultraviolet and the near-infrared regions (Yen, 2007). Luminescence is the general term used to describe both fluorescence and phosphorescence. These two types of luminescence have different characteristic in terms of their reaction times upon exposure of electromagnetic radiations.

Fluorescence has instant reaction upon exposure to radiations and its decay rapidly after the source of excitation removed. Meanwhile, phosphorescence has a unique ability to long afterglow radiation emission even after the source of energy has been removed (Valeur, 2001). There are two basic kinds of luminescence materials categorized as inorganic (phosphor) and organic (organoluminophosphors) luminescence.

Research in this field has established that the luminescent properties of phosphor materials can be altered and enhanced by doping the rare earth element as an activator into the structure of the host phosphor (Lakshmanan, 2008). Rare earth element such as europium have been widely used for energy saving lighting and display technologies, such as cathode ray tube (CRT), light-emitting diode (LED), organic light-emitting diode (OLED), plasma display panels (PDP) and scintillator (Ozawa, 2007; Ropp, 2004; Yen and Weber, 2004).

In the past, many chemical elements and compounds are being studied for their uses in luminescence. Among the substances being analysed, it seems rare earths to be most promising in terms of their high colour quality (Yu, 2011) and good energy efficiency. Unlikely this performance will be achieved without the use of rare earths from the current perspective.

1.2 Statement of Problem

Many researchers had found phosphors but the luminescence properties of alkaline earth phosphate/borophosphate are still interesting to study with respect to their potential applications in solid-state lighting, plasma display panel and optoelectronic devices (Huang *et al*., 2007; Li *et al*., 2008; Qin *et al.*, 2010). Researchers found that phosphate acted as a good host luminescent material because of its excellent properties such as thermal stability (Shinde *et al*., 2012; Tu *et al*., 2011) large band gap, moderate phonon energy and the high chemical stability (Wang *et al.*, 2011).

The considerable variety in the crystal structure of the phosphate compounds provided a great deal of objects for the study aiming at exploring new functional materials. However, phosphate is lower in chemical resistance and hygroscopic poses many obstructions on their commercial exploitation and usefulness (Hussin, 2002).

Previous studies showed various alkaline earth metals such as barium carbonate ($BaCO_3$), magnesium carbonate ($MgCO_3$), strontium carbonate ($SrCO_3$) and calcium carbonate ($CaCO_3$) improved dramatically the chemical durability (Moustafa, 1999). These metals led to the formation of Ba-O-P, Mg-O-P, Sr-O-P and Ca-O-P replaced the easily hydrosable P-O-P bonds (Shaw, 1988). In this respect, the addition of alkaline earth into phosphate networks is expected to yield materials with improved characteristics. Therefore, some improvements are needed such as by adding metal ions Ba^{2+} into the host for charge compensation.

The emission of luminescence base phosphorous is expected to be enhanced by the addition of rare earths. From the various lanthanide ions, europium ions are widely used as an activator in various host materials. It is expected that doping europium with oxidation +2 state will give rise to emission of ultraviolet to blue-light colour meanwhile europium with oxidation +3 state will emit red colour (Li *et al.*, 2013; Schüler *et al*., 2011; Tu *et al*., 2011; Yu, 2011). Divalent europium ions are potential candidates for white LED and ultraviolet LED (Yu *et al*., 2013). Hence, it

would be interesting to study the phosphate based phosphor doped with divalent europium ion.

Various method has been used for reduce the oxidation state of europium such as by using reduction gasses (Eg: H_2–N_2) and carbon. Reduction Eu^{3+} to Eu^{2+} in pure argon gas has been reported by Grandhe *et al*., 2011 in $NaCaPO_4$: Eu phosphor however there is not much information about this gas. To get more information, pure argon gas was using in this research to produce $BaBPO_5$: Eu^{2+} phosphor.

Luminescence of divalent europium ion in borophosphate phosphor was studied by many researchers (Komatsu *et al*., 2006; Liang *et al*., 2004; Blasse *et al*., 1969) but there is not much study was reported for $BaBPO_5$: Eu^{2+}. Up to our knowledge, there were no reported luminescence properties of $BaBPO_5$: Eu^{2+} was prepared by using solid state method in pure argon ambience. Hence, in this study the sample of phosphate-based phosphors will be added with various concentrations of europium and heated in pure argon atmosphere to obtain more information about their luminescence properties.

Even though there are many study of borophosphate was conducted, until to our knowledge, the SEM and infrared studies of $BaBPO_5$: Eu has not been reported before. Hence, it is interesting to conduct the studies of $BaBPO_5$ doped Eu by using SEM and FTIR to get further information of morphology and molecular structure.

1.3 Objective of Study

The objectives of this study are:

i) To synthesize $BaBPO_5$: Eu^{2+} phosphor with various europium concentration by solid state reaction under pure argon ambience.

ii) To determine the crystalline phase of the synthesized phosphor.

iii) To study morphology of synthesized phosphor.

iv) To determine the luminescence properties of $BaBPO_5$: Eu^{2+} phosphor.

1.4 Scope of Study

This is a study on luminescence properties of phosphate-based phosphor doped with different concentration of Eu^{2+} ions. The phosphors under study were sample of $BaBPO_5$: Eu^{2+} synthesized by solid state method under inert atmosphere (pure argon). Luminescence properties of samples were analysed by using Photoluminescence (PL) spectroscopy. Crystalline phase of the host material and its structure were determined using X-Ray Diffraction (XRD). The morphology of samples was analysed by using Scanning Electron Microscopy (SEM). The structural characterization of samples was analysed by Fourier Transform Infrared (FT-IR) spectroscopy.

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