STRUCTURAL AND LUMINESCENCE PROPERTIES OF BARIUM ORTHOSILICATE DOPED WITH EUROPIUM AND SAMARIUM IONS

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To my ayahanda and bonda.

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ABSTRACT

The development of white light-emitting diodes (WLEDs) in solid-state application is advanced by studying the properties of barium orthosilicate ceramics doped with europium and samarium. Ceramic materials based on the composition of $60BaO-30SiO_2-10Na_2O-4Eu_2O_3-3Sm_2O_3$ samples were successfully prepared via solid-state reaction method sintered at 1200 ºC for 5 hours. The structural and optical properties of the ceramics were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and photoluminescence (PL) spectroscopy. The XRD profiles indicated that the crystalline phase of synthesized samples was dominated by orthorhombic phase of Ba_2SiO_4 and SiO_2 monoclinic. An increment in Ba concentration intensified the crystallinity of the ceramics. The local network structures were represented by FTIR spectrum around 1220 – 1050 cm^{-1}, 930 cm^{-1}, and 1434 cm^{-1} assigned the presence of Si-O-Si, Si-O-Ba and SiO_3 unit, respectively. The results showed that the presence of Ba caused the breaking of network bonds and generated non-bridging oxygen (NBO) of Si-O-(Si, Ba). The optical properties of Ba_2SiO_4: Eu^{3+} were analysed by PL Spectroscopy which revealed a spectrum of five emission peaks for Eu^{3+} centred at 580 nm, 591 nm, 612 nm, 651 nm and 706 nm. Reddish-orange emission was originating from the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) transitions of Eu^{3+} under excitation of 394 nm. The ceramic with 4 mol% Eu^{3+} dopant exhibited the highest intensity for Ba_2SiO_4. The co-doping of Sm^{3+} was found to stimulate the enhancement in luminescence intensity and to sensitize the emission in Ba_2SiO_4: Eu^{3+}. The results suggested that the luminescence emission of this mechanism relied on the energy transferred from Sm^{3+} to Eu^{3+}. The optimum doping concentration of Sm^{3+} ions was determined to be 3 mol%. For Eu^{3+}/Sm^{3+} co-doped sample, down conversion luminescence spectra excited at 407 nm emitted five emission transitions of $^5D_0 \rightarrow {}^7F_J$ (J = 2, 4) and $^4G_{5/2} \rightarrow {}^6H_{J/2}$ (J = 5, 7, 9) respectively. Among them, the $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} and $^4G_{5/2} \rightarrow {}^6H_{7/2}$ of Sm^{3+} were the strongest transitions, leading to an intense red colour emission.

ABSTRAK

Suatu kemajuan dalam perkembangan diod pemancar cahaya putih dalam aplikasi keadaan-pepejal ialah dengan mengkaji sifat-sifat bahan seramik barium orthosilikat yang didopkan dengan europium dan samarium. Bahan seramik yang berdasarkan komposisi 60BaO-30SiO_2-10Na_2O-4Eu_2O_3-3Sm_2O_3 telah berjaya dihasilkan dengan menggunakan kaedah tindakbalas keadaan-pepejal yang disinter pada 1200 ºC selama 5 jam. Sifat struktur dan sifat optik seramik telah diciri menggunakan pembelauan sinar X (XRD), spektroskopi Fourier transformasi inframerah (FTIR) dan spektroskopi fotopendarcahaya (PL). Profil pembelauan sinar-X menunjukkan bahawa sampel yang telah disintesis telah didominasi oleh fasa orthorhombik Ba_2SiO_4 dan monoklinik SiO_2. Peningkatan kepekatan Ba menyebabkan penguatan pada penghabluran seramik. Struktur rangkaian tempatan yang ditunjukkan oleh spektrum FTIR di sekitar 1220 – 1050 cm^{-1}, 930 cm^{-1}, dan 1434 cm^{-1}, masing-masing menunjukkan kehadiran unit Si-O-Si, Si-O-Ba dan SiO_3. Hasilnya membuktikan bahawa kehadiran Ba telah menyebabkan pemutusan rangkaian ikatan dan menjana ketidaksambungan oksigen Si-O-(Si, Ba). Sifat optik Ba_2SiO_4: Eu^{3+} telah dianalisis menggunakan spektroskopi PL yang memaparkan spektra yang terdiri daripada lima puncak pancaran untuk Eu^{3+} yang berpusat di 580 nm, 591 nm, 612 nm, 651 nm dan 706 nm. Pancaran oren kemerah-merahan telah diterbit dari peralihan $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) di bawah pengujaan 394 nm. Seramik yang mempunyai 4 mol% Eu^{3+} memancarkan keamatan yang tertinggi untuk Ba_2SiO_4. Pendopan bersama Sm^{3+} didapati mendorong kepada peningkatan dalam keamatan pendarcahayaan dan memeka pancaran Ba_2SiO_4: Eu^{3+}. Kepekatan Sm^{3+} yang optimum telah dicapai pada 3 mol%. Keputusan tersebut mengusulkan bahawa mekanisma pancaran pendarcahaya ini bergantung kepada pemindahan tenaga daripada Sm^{3+} ke Eu^{3+}. Untuk sampel Eu^{3+}/Sm^{3+} yang didopkan bersama, spektra pendarcahaya penukaran turun yang diuja pada 407 nm memancarkan lima peralihan pancaran masing-masing $^5D_0 \rightarrow {}^7F_J$ (J = 2, 4) dan $^4G_{5/2} \rightarrow {}^6H_{J/2}$ (J = 5, 7, 9). Dalam kalangan peralihan tersebut, $^5D_0 \rightarrow {}^7F_2$ oleh Eu^{3+} dan $^4G_{5/2} \rightarrow {}^6H_{7/2}$ oleh Sm^{3+} adalah transisi terkuat yang membawa kepada pancaran warna merah yang berkeamatan tinggi.

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δ	-	Bending vibration
c	-	Velocity of light
d	-	Distance between atomic layers in crystal
E	-	Energy
h	-	Planck's constant
v	-	Frequency
θ	-	Angle
λ	-	Wavelength
$BaCO_3$	-	Barium carbonate
BaO	-	Barium oxide
Ba_2SiO_4	-	Barium orthosilicate
BO	-	Bridging oxygen
Eu_2O_3	-	Europium (III) oxide
FTIR	-	Fourier Transform Infrared
GSA	-	Ground state absorption
JCPDS	-	Joint Committee on Powder Diffraction Standards
LED	-	Light emitting diode
Na_2O	-	Sodium oxide
NUV	-	Near ultra-violet
NBO	-	Non-bridging oxygen
NR	-	Non-radiative
PL	-	Photoluminescence
RE	-	Rare-earth
Si	-	Silicon
SiO_2	-	Silicon dioxide

Sm_2O_3	-	Samarium (III) oxide
XRD	-	X-ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Rapidly advancing technology nowadays continually demands materials with more stringent specifications for each new application. In the past 50 years, scientists and manufacturers played a key role in the development of industrial ceramic (Bengisu, 2001). Today, ceramics become one of the most studied in materials groups. In view of undoubted number of publications in this domain, it takes a lot of skill to keep up with the improvement in ceramic materials, just as in another level. A major interest on ceramic was their outstanding in electrical properties and heat resistance. Till now, ceramic plays an important role either in economic or human's daily life.

Other than excellent in structural properties such as high strength and hardness, electrical conductor and corrosion resistance, one of most significant discoveries possible by ceramic materials is in luminescence field. Ceramic are not only well-known for their good thermal and mechanical properties, they have the potential to become a great luminescence material as well. Most crystalline ceramic are opaque which lead to enhancing the absorption efficiency of rare earth ions (Yang *et al*., 2008).

The most important is the luminescence host need to be stable crystal structure, high physical and chemical stability and high quantum efficiency (Barry, 1968). Alkaline earth silicate are regarded as appropriate host with stable crystallographic to accommodate luminescent ions, water-resistant property, high physical and chemical stability compared to phosphor based sulphide and strontium aluminates phosphor (Yamazaki *et al*., 1986). It is also easy to prepare and low cost. For those reasons, silicate host was attracting more attention in luminescent and long afterglow field (Liu *et al*., 2007) and significant attention had been paid on account of its multi-colour phosphorescence and resistance to acid, alkali and oxygen. Based on previous studies, the crystal structures and photoluminescence properties of $Ba_9Sc_2Si_6O_{24}$ orthosilicate host doped Ce^{3+}/Na^{+} and $(Ba_{1-x-y}Sr_yEu_x)_9Sc_2Si_6O_{24}$ were successfully investigated (Bian *et al*., 2012; Bian *et al.*, 2013). This compound found to be an efficient luminescent host material that is activated in the NUV region.

In order to prepare silicate host material, however, high temperature is needed for phase formation in the range 1300 ºC – 1500 ºC. According to Lin *et al*. (2003) $Ca_2MgSi_2O_7$: Eu, Dy, $Sr_2MgSi_2O_7$: Eu, Dy and $Ba_2MgSi_2O_7$: Eu, Dy were prepared via sintering at 1300 ºC for 3 hours. Therefore, silicate host need to cooperate with some chemical to decrease the operating temperature. As an alternative, addition of barium into silicate is implied to overcome the problem due to its low melting point compared to silicate. That makes it possible to prepare ceramic at lower temperature. On the other hand, barium presents a considerable interest with revelation in 1994. Wang *et al*. (1994) reported that the replacement of Ca^{2+} by Ba^{2+} ions in $Ca_3Sc_2SiO_{12}$ brought a new material with different crystal structure.

An efficient luminescence performance can be improved greatly by doping with suitable activator. An activator means that the doping material represented by either rare-earth ions, transition metal ions or some ions which are capable to achieve luminescent properties. This is referring to high brightness intensity and the emission of spectrum would be possible to be in the range of visible region. The emission in visible light is an attention-grabbing in luminescent study because this range is suitable in various applications like mercury vapour lamp, bar code scanning laser and LED as well.

Every doping ion has their emission characteristic for examples, Zn_2SiO_4: Mn^{2+} emission at 525 nm (green), $Ca_2P_2O_7$: Dy^{3+} emission at 480 nm and 575 nm (white) (Leverenze, 1968). Hence, doping materials are very important to determine the emission of the ceramic. Several host silicate doped with rare earth (R^{n+}) ions, either divalent or trivalent, have been proposed as commercial phosphors in tricolour fluorescent lamps, scintillators and so on (Leverenze, 1968). Based on previous reports, luminescent material based alkaline earth silicate doped with Eu^{3+} and Sm^{3+} ions were studied (Lin *et al*., 2011; Liu *et al*., 2012). Eu^{3+} and Sm^{3+} ions were widely used in developing new colour light sources (Lin *et al*., 2005) and red emission may be a candidate for application in white LED. Besides, the interest of both ions as doping material is that they performed a uniform distribution and well matrix arrangement for both Eu and Sm-doped. This contributes to the improvement of the optical homogeneity final product (Elisa *et al*., 2013).

Nevertheless, the introduction of trivalent metallic ions such as Sm^{3+} and Eu^{3+} into host crystal and as substitutes for a divalent metallic ion will result in charge unbalance. This could induce defects in sample structure and leads to the reduction of luminescence intensity (Wang *et al*., 2012). Therefore, the incorporation of alkali metal ions, Na_2CO_3 might compensate the charge unbalance. Consequently, distortion of lattice will reduce and enhance the intensity of luminescence (Li *et al*., 2009; Liu, *et al*., 2011; Yan *et al*., 2011). An appropriate charge compensation not only improves relative intensity but the colour purity as well. In addition, the introduction of Na ions does not change the sub-lattice structure around the luminescent centre. This can be evidence in XRD results (Xie *et al*., 2010). As reported by Kim and Park (2013), the used of alkali metal ions (Li_2CO_3) as a flux experimentally can reduce the heating temperature by about 250 ºC. Hence, it is expected that by way of introduce Na_2CO_3 will lower the heating temperature in this research.

1.2 Problem Statement

Host materials particularly, silicates, sulphides, aluminates and borates have drawn much attention due to their valuable application by means of developing to be potential luminescent materials. They are outstanding in structure and optical properties such as stable crystallography, long after-glow and high brightness. However, there has been less extensively reported on the structural network of barium orthosilicate. Despite this, it was reported that silicate based host material needed high preparation temperature in the range above 1300 ºC that limited its application (Gao *et al*., 2010; Wang *et al*., 2013; Min *et al*., 2014). Hence, in order to decrease the operation temperature, another chemical compound such as barium needs to be added into the host. Therefore, the structure features of the barium orthosilicate will be studied for future reference in order to understand more about the host material properties. Furthermore, the synthesis of Eu^{3+} and Sm^{3+} doped barium orthosilicate is aiming to explore the variation of the emission colour and will emphasize on the luminescence properties of these ceramics. In addition, the emission and quenching in luminescence are still subjects under study (Benz and Strunk, 2012).

1.3 Objectives of Study

The objectives of this study are:

i. To prepare a series of barium orthosilicate ceramics doped with Eu^{3+} and a series of Eu^{3+} and Sm^{3+} co-doped barium orthosilicate ceramics.

ii. To characterize the structural features of barium orthosilicate ceramic network.

iii. To determine the luminescence properties of barium orthosilicate ceramics doped with Eu^{3+} and the influence of Sm^{3+} as co-dopant.

1.4 Scope of Study

In order to achieve the objectives, the samples of ceramic based host material on composition of $60BaO-30SiO_2-10Na_2O$ doped with europium and samarium ions will be prepared by solid state reaction method. The phase and crystallinity of the synthesized compositions will be obtained by powder X-ray Diffraction (XRD) while the structure feature of samples will be measured using Fourier Transform Infrared (FTIR) spectroscopy. The emission spectra will be carried out from Photoluminescence (PL) instrument and determination based on down conversion mechanism of luminescence spectra.

1.5 Significant of Study

Several investigations have been done from the earlier study in the luminescent field. Researchers made a lot of discoveries of phosphor ceramic and the development of novel materials represents a new and fast evolving application of research in physics and industries. The purpose of this research is to find a ceramic based material of barium orthosilicate regarding the potential and promising structure and luminescence properties. The influence of dopant Eu^{3+} and Sm^{3+} co-dopant will enhance high intensity of luminescence of the samples. It will come out with great luminescent properties which are easy to prepare, increasing brightness and various applications, thus, this study will contribute and discover of luminescent materials that can emit visible emission for widely solid state lighting applications. This may help in new knowledge in luminescent industry and future study.

1.6 Thesis Outline

Preparation and characterization of europium and samarium doped silicate ceramic via solid state reaction method will be explained in this thesis. It comprises of five chapters. For Chapter 1, the background of the research briefly mentioned with emphasis on development of ceramic with respect to optical properties. On top of that, several sub topic including problem statement, objectives, scope of study and significance of the research as well as thesis outline.

Chapter 2 deals with some of theories related to luminescence such as its mechanism, energy transfer and emission spectra and basic information about the materials used in this study are also pointed out. Theory on the analysis works to characterize samples like XRD, FTIR and PL spectroscopy will be featured in this chapter.

Chapter 3 states the experimental and measurement techniques which consist of sample preparation and the apparatus used for both structural and luminescence analysis. The parameters and physical measurements are defined.

Chapter 4 is focused on the experimental results and discussion will be given in detail. The ceramic analysed using XRD and FTIR will lead to understanding of the crystallinity phase and structural involve in the host lattice. The effect of Eu^{3+} and Sm^{3+} will be emphasized on optical properties of the prepared samples via PL analysis.

Last but not least, Chapter 5 will firstly conclude the findings of this research. Comprised within the conclusion is a summary of the theory involved regarding to luminescent process. In consideration of the limitations in this research, suggestions for further research are outlined.

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