UNIVERSITI PUTRA MALAYSIA

STRUCTURAL AND OPTICAL PROPERTIES OF LOW COST ZINC SILICATE-BASED GLASS CERAMICS DOPED WITH EUROPIUM

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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STRUCTURAL AND OPTICAL PROPERTIES OF LOW COST ZINC SILICATE-BASED GLASS CERAMICS DOPED WITH EUROPIUM

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Chairman : Yap Wing Fen, PhD
Faculty : Institute of Advance Technology

To date, the demand for better light emitting diodes (LEDs) has led to growing interest in producing Zn_2SiO_4 based glass ceramic phosphors using waste materials. In this research, low cost Zn_2SiO_4:$x$$Eu^{3+}$ phosphors were prepared based on a solid state method using recyclable glass wastes as silica source. The influence of Eu^{3+} ions (x = 0, 1, 2, 3, 4 and 5 wt.%) and the effect of sintering temperatures, ranging from 600 to 1000 °C on the structural, morphological and optical properties of the phosphors were also investigated using X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, Ultraviolet-visible near infrared (UV-Vis-NIR) spectroscopy and Photoluminescence (PL) spectroscopy. These glass ceramics showed the increasing densities with increasing Eu^{3+} and sintering temperature. Structural investigation using XRD had revealed that the higher intensities of the diffraction peaks were due to sintering temperatures. Furthermore, their diffraction peaks had slightly shifted to lower diffraction angles when the dopant's concentration was increased. The morphologies from FESEM analysis showed the formation of densely packed grains and smooth surfaces with the increment of sintering temperatures and addition of dopants. FTIR spectra showed that the progression of sintering temperature has narrowed the broad bands of SiO_4 and ZnO_4 at 1000 °C. All the broad bands were reduced to smaller bands after the addition of dopant. Additionally, the effects of sintering temperatures and dopants on the samples were apparent on the Raman spectra, which showed the narrow width of Raman lines and the shifted energy region in the spectrum. Most importantly, the largest optical band gaps of the samples were found at the highest sintering temperature. Meanwhile, Eu^{3+} doped samples have shown the largest optical band gap at 1000 °C upon the examination of the Moss-Burstein effect. Results for the photoluminescence showed red luminescence emissions at 600 nm due to Eu^{3+} transitions under 400 nm excitation. It was observed that sintering temperatures of 900 and 1000 °C have decreased the intensity of emission, while the highest doping concentration of 5 wt.% of Eu^{3+} has shown the highest emission intensity of the phosphors. Apart from that, waste silica sources have proven to have excellent crystallinity, surface morphology, optical band gap and

emission intensity for obtaining red emitting phosphors, which could also be useful for white LEDs.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains.

STRUKTUR DAN SIFAT OPTIK BAGI SERAMIK KACA KOS RENDAH BERASASKAN ZINK SILIKA DIDOPKAN EUROPIUM

Oleh

NUR ALIA SHEH OMAR

Ogos 2016

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Sehingga kini, permintaan untuk diod pemancar cahaya (LEDs) yang lebih baik telah membawa peningkatan kepentingan dalam menghasilkan zink silika seramik kaca fosfor dengan menggunakan sisa bahan. Dalam kajian ini, bahan kos rendah Zn_2SiO_4:$x$$Eu^{3+}$ telah disediakan berdasarkan kaedah keadaan pepejal menggunakan sisa kaca yang boleh dikitar semula sebagai sumber silika. Pengaruh Eu^{3+} ion yang berbeza (x = 1, 2, 3, 4 and 5 wt.%) dan kesan suhu pembakaran daripada 600 ke 1000 °C ke atas struktur, morfologi, dan sifat optik telah dikaji dengan menggunakan pembelauan sinar-X (XRD), mikroskop pelepasan bidang imbasan electron (FESEM), spektroskopi inframerah (FTIR), spektroskopi Raman, spektroskopi ultraungu cahaya nampak inframerah (UV-Vis-NIR) dan spektroskopi kefotopendarcahayaan (PL). Seramik kaca telah menunjukkan peningkatan ketumpatan dengan penambahan Eu^{3+} dan suhu pembakaran. Kajian struktur menggunakan XRD mendapati pembelauan puncak dengan keamatan yang tinggi disebabkan peningkatan suhu pembakaran. Tambahan pula, pembelauan puncak telah beralih sedikit ke sudut pembelauan yang lebih rendah apabila kepekatan pendopan meningkat. Morfologi daripada analisis FESEM menunjukkan pembentukan butiran yang padat dan permukaan yang rata dengan peningkatan suhu pembakaran dan penambahan pendopan. Spektra FTIR telah menunjukkan peningkatan suhu akan mengecilkan jalur lebar SiO_4 dan ZnO_4 pada 1000 °C. Semua jalur lebar dikurangkan kepada jalur yang lebih kecil selepas penambahan pendopan. Tambahan lagi, kesan suhu pembakaran dan pendopan ke atas sampel telah kelihatan di spektra Raman yang mana menunjukkan ketirusan lebar jalur Raman dan peralihan kawasan tenaga di dalam spektrum. Paling utama, jurang jalur optik yang besar telah dijumpai pada suhu pembakaran yang paling tinggi. Manakala, sampel yang didopan Eu^{3+} telah menunjukkan jurang jalur optik yang besar di 1000 °C disebabkan kesan ‘Moss-Burstein’. Keputusan kefotopendarcahayaan telah memberikan pendarcahayaan pancaran merah di 600 nm berikutan peralihan Eu^{3+} di bawah pengujaan biru. Ia juga telah dilihat, suhu pembakaran daripada 900 dan 1000 °C telah mengurangkan keamatan pancaran, manakala kepekatan pendopan paling tinggi, 5 wt.% daripada Eu^{3+} telah menunjukkan keamatan pancaran fosfor yang paling tinggi. Selain itu, sisa sumber silika telah terbukti mempunyai ciri penghabluran, permukaan morfologi, jurang jalur optik dan keamatan pancaran yang baik bagi

menghasilkan pemancar merah fosfor yang boleh digunakan untuk diod pemancar cahaya putih.

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I certify that a Thesis Examination Committee has met on 16 August 2016 to conduct the final examination of Nur Alia binti Sheh Omar on her thesis entitled "Structural and Optical Properties of Low Cost Zinc Silicate-Based Glass Ceramics Doped with Europium" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS AND SYMBOLS

Al_2O	Aluminium Oxide
CaO	Calcium Oxide
COD	Crystallography Open Database
Dy^{3+}	Trivalent Dysprosium Ion
Eu^{3+}	Trivalent Europium Ion
Fe_2O_3	Ferric oxide
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
ICDD	International Centre for Diffraction Data
ICSD	Inorganic Crystal Structure Database
JCPDS	Joint Committee on Powder Diffraction Standards
K_2O	Potassium Oxide
MgO	Magnesium Oxide
Na_2O	Sodium Oxide
PL	Photoluminescence
SiO_2	Silica Oxide
SLS	Soda Lime Silica
Sm^{3+}	Trivalent Samarium Ion
Tb^{3+}	Trivalent Terbium Ion
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
Zn_2SiO_4	Zinc Silicate / Willemite
ZnO	Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1 Zinc Silicate

Recently, researchers have shown increased interests in the fabrication of oxide based on inorganic silicate phosphors that have efficient luminescence and chemical stability for advanced phosphor and photonic applications. Among these inorganic silicate phosphors, zinc silicate (Zn_2SiO_4), or also known by its mineral name, willemite, is one of the earliest discoveries during 1829 at Moresnet, La Calamine, Belgium by Armand Lévy (Lévy, 1843; Schneider *et al.*, 2008). The name willemite was dedicated to the King of the Netherlands, Willem I of Orange-Nassau (Takesue *et al.*, 2009). This material is one of the zinc ore minerals that have a phenakite structure, which belongs to the group of orthosilicates with a trigonal-rhombohedral symmetry (Simonov *et al.*, 1977; Tarafder *et al.*, 2014; Rao *et al.*, 2014). The average density of willemite is 4.05 kg/m^3, while its colour variation ranges from transparent to red-brown and black (Brugger *et al.*, 2003; Hitzman *et al.*, 2003). To date, studies on willemite phosphor are focused on its occurrence, its crystallography, its luminescence, and its application as an industrial material. In terms of crystallography, the ZnO-SiO_2 system produces three different phases at high temperature reactions, namely, α, β, and γ-Zn_2SiO_4. The α-Zn_2SiO_4 phase, which melts at 1512 °C, is known as the stable phase of orthosilicate or neosilicate in nature. It consists of isolated Zn-O tetrahedrons and Si-O tetrahedrons (Bunting, 1930; Ingerson *et al.*, 1948). Additionally, willemite is a well-known as the nature of the green mineral fluorescence. Prior to the development of halophosphor in 1942, the synthetic Franklin's willemite was taken down to exhibit green luminescence when it was activated with divalent manganese (Mn^{2+}) luminescence center. Ever since, this synthetic willemite was used as a phosphor in fluorescent lamp, neon discharge lamps, black and white television, and many other displays and lighting devices.

1.2 Rare Earth

Recent developments in luminescent materials have led to a high interest in inorganic materials doped with rare earth ions. Such material can be utilized in various display devices, such as flat panel displays, plasma display panel, field emission display, light emitting display, sensors and lasers (Huong *et al.*, 2012; Shi *et al.*, 2013; Janković *et al.*, 2014; Zhang *et al.*, 2014). The strength, toughness and luminescence efficiencies of the host materials are enhanced by adding small concentrations of rare earth oxides (also known as dopants) (Guanming *et al.*, 2007; Li *et al.*, 2012). Generally, rare earth elements are made up of two series elements, such as lanthanide and actinide series. The lanthanide series includes elements with atomic numbers from 57 to 71. These elements mainly exhibit the +3 oxidation state, and are usually used in crystalline compounds, superconductors and permanent magnets. Furthermore, these rare earth elements can also be identified by the well shielding of the unpaired electrons in the

4*f* orbital with the outer $5s^2$ and $5p^6$ orbitals. Because of their specific electronic configurations, these elements possess good luminescent characteristics with high emission efficiency and high color purity (Huang *et al.*, 2006; Krsmanović *et al.*, 2009). Among the lanthanide elements, trivalent europium (Eu^{3+}) has attracted much attention as a luminescence activator ion with a reddish emission bands from $^5D_0 - {}^7F_2$ transitions. This element traditionally occupies the dominant role of active ions in many optical spectroscopies due to the large number of absorption and sharp emission bands arising from the transition between their energy levels (Shionoya and Hirano, 1968). Other than that, europium is an effective material that can be found in two oxidation states, i.e. Eu^{2+} and Eu^{3+} depending on the preparation purpose. It is the only lanthanide ion with the ground state, J = 0, with exceptional restrictions which exist on the induced electric-dipole transitions that originated from the ground state (Rao *et al.*, 2013a). Furthermore, it is also a vital luminescent activator ion due to its reddish emission that can be utilized in various optical devices such as electroluminescent devices, optical amplifiers, and lasers (Mesfar *et al.*, 2013).

1.3 Soda Lime Silica Glass

To date, various researches have proposed the diversification of glass ceramic production by using recyclable by-products as raw and starting materials. The recyclable by-products include zinc-hydrometallurgy waste (Pelino, 2000), basaltic rocks (Bickford and Jantzen, 1986; Khater *et al.*, 2012), refining of silica sand and kaolin clay (Toya *et al.*, 2004), flu gas (Kim and Kim, 2004), steel slag (He *et al.*, 2012) and panel glass (Bernado *et al.*, 2007). In addition, soda lime silica (SLS) glass from recyclable bottles has also renewed the interest of 90% of the world's glass manufacturers (Matori *et al.*, 2010). SLS glasses that consist mainly of silicon dioxide (SiO_2), sodium oxide (Na_2O) and calcium oxide (CaO) have good glass-forming nature compared to several other conventional systems (Chimalawong *et al.*, 2010; Marinoni *et al.*, 2013). Previous studies on SLS glass have shown that it has fine optical and mechanical properties, such as good chemical stability, good durability, low melting point, high ultraviolet transparency, high surface damage threshold and good rare earth ion solubility (Xu *et al.*, 2004; Qiao *et al.*, 2006; Chimalawong *et al.*, 2012). The compositions of SLS glass using EDXRF are presented in Table 1.1 (Zaid *et al.*, 2012).

Table 1.1: Analysis of chemical composition of SLS glass using EDXRF (Zaid *et al.*, 2012).

Elements	Wt.%
SiO_2	69.5
CaO	11.3
Na_2O	12.5
Al_2O_3	2.8
K_2O	1.5
MgO	2.0
Fe_2O_3	0.2
B_2O_3	0.1
BaO	0.1

1.4 Glass Ceramic

In 1953, an accidental overheating of a glass furnace at 900 °C by Stanley Donald Stookey has led to the discovery of glass ceramics. Small crystals were found in the amorphous material, which can prevent cracks from propagating through the glass after the glass is overheated (Stookey, 2000). The obtained glass ceramics are known as microcrystalline solids that are produced by the controlled crystallization (devitrification) of a glass (Beall, 1992). The crystallization of a glass consists of melting, quenching, and heating processes that can form a predominantly crystalline ceramic. The basis of controlled crystallization lies in the efficient internal nucleation, which allows the development of fine-grained polycrystalline materials without voids, micro cracks, or other porosity. Glass ceramics are easily manufactured using high speed plastic forming processes (e.g. pressing, blowing, rolling) to create complex shapes, which are essentially free of internal inhomogeneity. Glass ceramics are favoured due to their high mechanical strength, low coefficients of thermal expansion, high temperature stability, high chemical durability, low dielectric constant and loss, as well as high resistivity (McMillan, 1974). Thus, a wide range of glass ceramic materials with tailored properties have been developed and used as cook wares, electrical insulators and substrates, building materials, architectural cladding, in medicine and dentistry, and as optical materials (Goncalves *et al.*, 2002; Callister and Retwisch, 2014).

1.5 Problem Statement

Numerous studies have focused on the preparations and optical properties of inorganic luminescent materials (Tang *et al.*, 2008; Vijaya and Jayasankar, 2013; Rojas *et al.*, 2014; Sudharani *et al.*, 2014; Wu *et al.*, 2014). Zn_2SiO_4 is one of the ideal hosts for luminescent materials (Joly *et al.*, 2007; El Mir *et al.*, 2007) due to its chemical stabilities and high luminescent efficiencies (Zhang *et al.*, 2000). Consequently, Zn_2SiO_4 doped with transition metal ions, such as manganese (Kwon and Kim, 2005), titanium (Guo *et al.*, 2006), vanadium (El Ghoul *et al.*, 2012), and nickel (Babu and Buddhudu, 2014a) have been used extensively as efficient luminescent materials for lamps and cathode ray tubes (CRTs). However, growing interests on white light-emitting diodes (w-LEDs) due to their high color rendering, long life span and low power consumptions have attracted much attention towards developing rare earth doped Zn_2SiO_4 phosphors (Shi *et al.*, 2006; Raju *et al.*, 2010; Yang *et al.*, 2013). The bright colour luminescence of rare earth doped materials can also be observed from the narrow characteristics of the emission bands in the optical spectra (Liu *et al.*, 2000). Thus, an intensive research is needed on Zn_2SiO_4 doped with rare earth ions, such as Tb^{3+}, Eu^{3+} and Ce^{3+} (Zhang *et al.*, 2001; Zhang *et al.*, 2003) that can produce excellent luminescent in green, red and blue emissions, respectively.

Numerous studies have been conducted to develop Zn_2SiO_4 doped with rare earth ions using high purity silica (SiO_2) source as a raw material. Such productions are costly since SiO_2 is quite expensive and it has a melting point of higher than 1700 °C. Previous studies have also reported that a large amount of energy consumption is required to prepare Zn_2SiO_4 which covers the process of melting, heating and cooling. Bunting *et al.* (1930) and Patrascu *et al.* (2009) have reported that the melting point for Zn_2SiO_4 is 1498 °C. Further optimization of this method is needed to produce low cost Zn_2SiO_4. Therefore, waste SLS glass was chosen to replace the high purity silica source. SLS glass is cheaper but able to exhibit low melting point, good chemical stability, high transparency, high thermal stability, and good solubility for rare earth ions. Other than that, using waste SLS glass helps to reduce the quantity of solid waste and thus, helps preserve the environment as well.

The solid state method (Natarajan *et al.*, 2005) and several chemical methods, which include the sol-gel method (Babu and Buddhudu, 2013), polymer precursor method (Su *et al.*, 1996), spray pyrolysis method (Kang and Park, 2000), hydrothermal method (An *et al.*, 2010) and sonochemical method (Masjedi-Arani and Salavati-Niasari, 2016) have been used to fabricate Zn_2SiO_4. Among these methods, the solid state method is simpler for producing large scale Zn_2SiO_4 compared to the chemical methods (Lakshmanan, 2012; Wong *et al.*, 2013; Li *et al.*, 2014; Tamrakar *et al.*, 2014). This is because the chemical methods require complicated steps, high cost equipment and long preparation periods (Khobragade *et al.*, 2013).

In view of these factors, it is of interest to develop novel $Zn_2SiO_4:Eu^{3+}$ using the solid state method. The structural and optical properties of $Zn_2SiO_4:Eu^{3+}$ are investigated.

1.6 Objectives of the Study

The objectives of this research are summarized as follows:

1) To synthesize $Zn_2SiO_4:Eu^{3+}$ from waste SLS glass, ZnO and Eu_2O_3 using solid state method.
2) To study the effect of sintering temperatures towards structural and optical properties of $Zn_2SiO_4:Eu^{3+}$.
3) To evaluate the effect of Eu_2O_3 doping towards structural and optical properties of $Zn_2SiO_4:Eu^{3+}$.

1.7 Scopes of the Study

The scopes of the study are stated as follows:

1) Zinc silicate doped with europium ions, $Zn_2SiO_4:Eu^{3+}$ was prepared from waste SLS glasses, ZnO and EuO powders. The following stoichiometric equation, $(ZnO_{0.5}SLS_{0.5})_{1-y}$ $(Eu_2O_3)_y$ where y = 0, 0.01, 0.02, 0.03, 0.04 and 0.05, was applied in the conventional solid state method. All starting materials were used as reference materials.
2) Sintering temperatures to produce $Zn_2SiO_4:Eu^{3+}$ glass ceramics were varied from 600 °C to 1000 °C.
3) The density and chemical compositions of $Zn_2SiO_4:Eu^{3+}$ were analyzed using an electronic densitometer and XRF analysis.
4) The structural properties, which include phase structure, bonding formation and surface morphology were characterized using XRD, FESEM, FTIR, and Raman analysis.
5) The optical properties, which include absorption, optical band gap and luminescence intensity of the samples were measured using UV-Vis-NIR and Photoluminescence spectroscopy.

1.8 Outline of Thesis

This thesis begins with Chapter 1, with an introduction to zinc silicate with the addition of doping ion, trivalent europium ions. Previous and current researches by other researchers are reviewed in Chapter 2. Then, the methods and instruments that were used to characterize the properties of zinc silicate doped europium ions are comprehensively explained in Chapter 3. The results, which include the effect of europium ions doping and sintering temperatures towards the physical, structural and optical properties of zinc silicate are analyzed and discussed in Chapter 4. Finally, the conclusion of the study and recommendations for future work are given in Chapter 5.

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