UNIVERSITI PUTRA MALAYSIA

SYNTHESIS, STRUCTURAL AND OPTICAL PROPERTIES OF COBALT (II) DOPED ZINC SILICATE VIA SOL-GEL METHOD

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By

NORHAFIZAH BINTI MOHD RASDI

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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November 2017

Chairman : Yap Wing Fen, PhD
Faculty : Institute of Advanced Technology (ITMA)

Zinc silicate (Zn_2SiO_4) has been distinguished as a competent host matrix for dopant transition and rare earth ion for efficient luminescence properties in red, green and blue spectral zones. The high demand of optical based materials for future development in light emitting diode (LED) and display panels has led to growing interest in producing Zn_2SiO_4 based glass ceramic via sol-gel method. In this researched work, the physical and optical properties of cobalt (II) doped zinc silicate were studied in detail. The sample was prepared by the sol-gel method at different compositions and heated at different heat treatments in the furnace. The preparation began with 2:1 mole ratio of Zn: SiO and with a different mole ratio of cobalt (II) doped (0, 1, 2, 3, 4 and 5 mol%) and the sample powder underwent heat treatment (600, 700, 800, 900 and 1000 °C) processes. The structural, morphological, and optical properties of cobalt (II) doped zinc silicate were studied in detail by using X-Ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), ultra-violet visible spectroscopy (UV-Vis), and photoluminescence spectroscopy (PL). XRD indicates that the formation of zinc oxide changes to zinc silicate (β-Zn_2SiO_4 and α-Zn_2SiO_4) as the sintering temperature increases from 600 to 1000 °C. Furthermore, as the dopant increases, the intensity of the sample also increases. This indicates that the crystallinity increases as the temperature and dopant increases. FESEM observation shows the average grain size increased with the increase of sintering temperature and when the dopant content increases the sample particle is more agglomerate and compact. The morphological properties show that the grain size of the samples increases as the heat treatment and dopant increases which leads to the increase in its growth rate. The FTIR result revealed the presence of Si-O-Si, ZnO_4 and SiO_4 vibrations in the sample. The UV-Vis study shows that, as the sintering temperature increase, the band gap energy tends to increase due to the improvement of the crystallinity and quantum size effect, while the decreasing band gap due to the separation energy of electron-hole pair. Meanwhile, as the dopant increases the band gap tends to decrease due to the involvement of non-bridging oxygen in the sample particle. The emission of photoluminescence spectra of cobalt doped zinc silicate powder after the sample was excited at a wavelength of 350 nm shows emission at 3 different peaks which were two

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blue emissions (420 and 480 nm) and green emission (525 nm). All peaks can be associated with d $\rightarrow$ d transition Co^{2+} from $^4A_2 \rightarrow {}^4T_1$ (^4P). In summary, it can be concluded that the sample of cobalt doped zinc silicate was successfully synthesized via sol-gel method and from the characterization, this shows that the sample can be suitable for optical devices.

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SINTESIS, SIFAT STRUKTUR DAN OPTIK ZINK SILIKA DIDOPKAN KOBALT (II) MELALUI KAEDAH SOL-GEL

Oleh

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Zink silika (Zn_2SiO_4) sebagai satu hos matriks yang kompeten bagi pendopan ion peralihan dan nadir bumi untuk sifat-sifat pancaran yang cekap dalam zon spektrum merah, hijau dan biru. Permintaan yang tinggi dalam bahan-bahan berasaskan optik untuk pembangunan masa depan dalam diod pemancar cahaya (LED) dan panel paparan telah membawa kepada penghasilan Zn_2SiO_4 berasaskan kaca seramik melalui kaedah sol-gel. Dalam kerja penyelidikan ini, sifat-sifat fizikal dan optik kobalt (II) didopkan zink silika telah dikaji secara terperinci. Sampel telah disediakan oleh kaedah sol-gel pada komposisi yang berbeza dan dipanaskan pada rawatan haba yang berbeza dalam relau. Persediaan dimulakan dengan nisbah mol 2:1 Zn:SiO dan dengan nisbah mol yang berbeza pendopan kobalt (II) (0, 1, 2, 3, 4 dan 5 mol%) dan serbuk sampel menjalani proses rawatan haba (600, 700, 800, 900 dan 1000 °C). Sifat-sifat struktur, morfologi, dan optik kobalt (II) zink silika yang didopkan telah dikaji secara terperinci dengan menggunakan pembelauan X-Ray (XRD), mikroskop imbasan pancaran medan elektron (FESEM), jelmaan Fourier infrared spektroskopi (FTIR), ultra-violet spektroskopi yang boleh lihat (UV-Vis), dan kefotopendarcahayaan spektroskopi (PL). XRD menunjukkan bahawa pembentukan perubahan zink kepada oksida zink silika (β-Zn_2SiO_4 and α-Zn_2SiO_4) apabila suhu pembakaran meningkat dari 600-1000 °C. Tambahan pula, apabila dopan meningkat, keamatan sampel juga meningkat. Ini menunjukkan bahawa pengkristalan meningkatkan dengan suhu dan pendopan. Pemerhatian FESEM menunjukkan purata saiz butiran meningkat dengan peningkatan suhu pembakaran dan apabila kandungan pendopan meningkat sampel zarah adalah lebih menggumpal dan padat. Pemerhatian morfologi menunjukkan bahawa saiz butiran sampel meningkat apabila rawatan haba dan pendopan meningkat yang membawa kepada kenaikan kadar pertumbuhannya. Hasil FTIR mendedahkan kehadiran Si-O-Si, ZnO_4 dan SiO_4 getaran dalam sampel. Kajian UV-Vis menunjukkan bahawa, kenaikan suhu pembakaran, menyebabkan jurang jalur tenaga meningkat disebabkan oleh peningkatan pengkristalan sampel dan kesan saiz kuantum, manakala jurang jalur berkurangan adalah kerana tenaga pemisahan oleh pasangan elektron-lubang. Sementara itu, peningkatan pendopan mengurangkan jurang jalur disebabkan oleh penglibatan oksigen tidak-rapat dalam sampel zarah. Selepas merangsang sampel pada panjang gelombang 350 nm, pancaran

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kefotopendarcahayaan spektrum oleh serbuk kobalt terdop zink silika menunjukkan pancaran di 3 puncak yang berbeza iaitu pancaran biru (420 dan 480 nm) dan pancaran hijau (525 nm). Semua puncak boleh dikaitkan dengan peralihan d → d Co^{2+} dari $^4A_2$ → $^4T_1$ (^4P). Secara kesimpulannya, penyediaan kobalt didopkan zink silika melalui kaedah sol-gel berjaya dan dari pencirian menunjukkan bahawa sampel ini sesuai untuk peranti optik.

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I certify that a Thesis Examination Committee has met on 8 November 2017 to conduct the final examination of Norhafizah binti Mohd Rasdi on her thesis entitled "Synthesis, Structural and Optical Properties of Cobalt (II) Doped Zinc Silicate via Sol-Gel Method" 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

AFM	Atomic Force Microscope
Ar	Argon
Co/Co^{2+}	Cobalt/Cobalt (II) Ion
CoO	Cobalt Oxide
Cu^{2+}	Copper (II) Ion
EDX	Energy Dispersive X-Ray
Er^{3+}	Trivalent Erbium Ion
EtOH	Ethanol/ethyl alcohol
Eu^{3+}	Trivalent Europium Ion
Fe/Fe^{3+}	Ferum
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infra-Red
H_2	Hydrogen Gas
HCl	Hydrochloric Acid
HDAC	Hydrothermal Diamond Anvil Cell
HNO_3	Nitric Acid
ICDS	Inorganic Crystal Structure Database
JCPDS	Joint Committee on Powder Diffraction Standards
$LiNO_3$	Lithium Nitrate
Li_2MoO_4	Lithium Molybdate
Mn/Mn^{2+}	Manganese (II) Ion
$Mn(NO_3)_2$	Manganese (II) Nitrate
NBO	Non Bridging Oxygen
NIR	Near Infra Red
NH_3	Nitric Acid
NH_4OH	Ammonium Hydroxide
N_2	Nitrogen Gas
Ni^{2+}	Nickel (Ii) Ion
O_2	Oxygen Gas
pH	Potential of Hydrogen
PL	Photoluminescence
RE	Rare Earth
SEM	Scanning Electron Microscope
SLS	Soda Lime Silica
SiO_2	Silica Oxide
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl Orthosilicate
TGA/DTA	Thermal Gravimetric Analysis/Differential Thermal Analysis
TiO_2	Titanium Oxide
TM/TM^{2+}	Transition Metal
XRD	X-Ray Diffraction
V	Vanadium
$ZnCl_2$	Zinc Chloride
$Zn(NO_3)_2$	Zinc Nitrate
Zn_2SiO_4	Zinc Silicate
ZnO	Zinc Oxide

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

The development of physics and characterization techniques today has significant contributions to the production of advanced materials. Nowadays a great deal of interest is focused on synthesizing method and optical properties of variety oxide-based phosphors for future developments due to the extensive demand in optical base materials for its various application in devices such as plasma displays, fluorescent display tubes, cathode ray tubes, and light emitting diodes (LED) (Blasse and Grabmaier, 1994; Zhang, 2006). For example, the host matrix zinc silicate has been identified as a very suitable host matrix for many transition metal and rare earth dopant ions for the efficient luminescence. It was first found by Armand Lévy in 1829 and named willemite after the ruler of the Netherlands (1813-1840), King Willem I (Schneider *et al.*, 2008).

Zinc silicate (Zn_2SiO_4), also widely known as willemite, is an important ore of zinc that belongs to the phenakite group which its orthosilicate ion has trigonal-rhombohedral symmetry (Rao *et al.*, 2014; Tarafder *et al.*, 2014). Willemite is an ideal phosphors host material due to its chemical stability and transparency in the ultraviolet-visible range (Zeng *et al*., 2009). Zn_2SiO_4 is the most practical phosphors which exist in the form of various phases (polymorphs) crystallizing in different space groups (Syono *et al.*, 1971). It is highly fluorescent (green) under shortwave ultraviolet light. Among all polymorphs, the α-Zn_2SiO_4 phase is common practical crystallizing with rhombohedral lattice structure (R3 space group) which can emit green light (Cho *et al*., 2003; Sivakumar *et al.*, 2012). Transition metal (TM)- or rare earth (RE)-doped Zn_2SiO_4 practical phosphors can emit different blue, green or red light depending on its ion incorporated and phase (α-, β-Zn_2SiO_4) that forms in the sample (Chang *et al.*, 1980; Ramakrishna *et al.*, 2014; Yang *et al.*, 2004). The α-Zn_2SiO_4 is a much stable phase compared to β-Zn_2SiO_4 where the β-phase has an orthorhombic crystal structure. For this reason, a variety of host materials for TM dopants have been analyzed and described in the literature regarding diverse practical applications (El Ghoul *et al.*, 2013; Seo *et al.*, 2009; Tsai *et al.*, 1991).

1.2 Transition Metal

At present, Zn_2SiO_4 doped TM is devoured in high volumes for the most advanced TV and flat display panel (FDP) technologies because of its steady radiance efficiency, high shading virtue, as well as high chemical and thermal stability (Diao *et al.,* 2011; Liu *et al.*, 2010; Yocom *et al.*, 1996). Various studies done on Mn^{2+} doped Zn_2SiO_4 is due to its ability to emit green emission, which has been used in cathode ray tube and electroluminescent devices and advanced technology displays (Kretov *et al.*, 2012; Lin *et al.*, 1999; Ouyang *et al.*, 1996; Yang *et al.*, 2003). Mn^{2+} has similar oxidation and

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valence states with Zn^{2+} and could be well distributed as the substituent of Zn^{2+}, therefore encouraging green emission to the host matrix (Selomulya *et al.*, 2003). Due to this case, TM-doped Zn_2SiO_4 has attracted extensive research interest in recent years (El Hadri *et al.*, 2015; Lukić *et al.*, 2008; Ozel *et al.*, 2010). Transition metals are well-known as optically active dopants in crystalline host because they fluoresce broadly in the near-infrared and also yield stronger optical activity in a crystalline, compared to amorphous glass (Pinckney and Beall, 2001).

1.3 Glass Ceramic

Glass-ceramics have an amorphous phase and one or more crystalline phases and are produced through controlled nucleation and crystallization of glass. Glass-ceramics have the fabrication advantage of glass, as well as special properties of ceramics (Alekseeva *et al.*, 2010). It is in contrast to spontaneous crystallization, which is usually not wanted in glass manufacturing. Glass ceramics were first found by Stanley Donald Stookey who was accidentally overheating of a glass at 900 °C. The material had crystallized completely after overheating such that it could not flow like amorphous glass usually does. It was harder than carbon steel yet lighter than aluminum – in short shatterproof (Stookey, 2000). In glass-ceramics, excellent transparency can be obtained when the crystal sizes are much smaller than the wavelength of light or in which the crystalline phases and glass have closely matched indices of refraction and the crystals have low birefringence (Beall and Pinckney, 1999). In many cases, glass ceramic can also allow the growth in the glass of crystals which are difficult or impossible to obtain in single crystal form. Glass ceramic are favored due to their high-temperature stability, high strength, toughness, high chemical durability, low dielectric constant and loss, as well as high resistivity. Therefore, due to its properties, glass ceramic has become well-known for use in glass-ceramic cookware and bakeware, as high-performance reflectors for digital projectors, as building materials in construction and architectural components, and optical materials (Ferrari, 2015; Rawlings *et al.*, 2006).

1.4 Problem Statement

Willemite ceramics have been considered to be technologically significant because of its electrical conductivity, good mechanical strength, thermal conductivity, and low coefficient of thermal expansion (Babu *et al.*, 2014). A great deal of interest has been focused on the preparation and optical properties of willemite phosphor for their potential application in various display panels. Meanwhile, TM ions doped Zn_2SiO_4 for future visible light emitting diode (LED) are critically reviewed from the degree point of their chemical durability, physical properties, phase transformation, optical properties, luminescent, thermal and mechanical properties, and elasticity compared with the other commercial products (Babu *et al.*, 2014; Jüstel, 2003; Kang *et al.*, 2000; Kretov *et al.*, 2012). Thus, an intensive study is needed on Zn_2SiO_4 doped TM, such as Mn^{2+} (Liu *et al.*, 2010; Wang *et al.*, 2006), Co^{2+} (Brunold *et al.*, 1996), Pb^{2+} (Wang *et al.*, 2005), Bi^{3+} (Yang *et al.*, 2003) and, Fe^{2+} (Lin *et al.*, 1994). A literature survey showed that there are only a few reports on the study of cobalt (II) doped Zn_2SiO_4.

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Zn_2SiO_4, following its discovery, have made researchers more interested towards its preparations, occurrence, crystallography, luminescence, and its application as an industrial fabric. Currently, researchers are focusing on building up new strategies for preparing Zn_2SiO_4 phosphor without utilizing high temperature solid-state reaction paths so that they can develop the sample under low energy processes for future advancement (Lu *et al.*, 2011; Machida *et al.*, 2011). There are a few methods being employed in parliamentary procedures to produce the sample such as hydrothermal method (Kodaira *et al.*, 1975; Pozas *et al.*, 2005; Suino *et al.*, 2013), spray pyrolysis (Gabás *et al.*, 2009), and supercritical method (Takesue *et al.*, 2010) however those methods involve high energy, complicated steps, high-cost preparations and long preparation periods. In addition, new applications utilizing fine or uniform materials may be discovered and developed in the future. Sol-gel method (Krsmanović *et al.*, 2009; Razavizadeh and Ghorbani, 2016) is one of the methods widely in use nowadays because high purity particles can be produced, the particle shape and final form of the sample can be controlled, the ability to improve the particle size dispersion, or evolve low temperature routes. It is of interest to develop novel Zn_2SiO_4: Co^{2+} using sol-gel method. The structural and optical properties of cobalt (II) doped Zn_2SiO_4 are thus investigated.

1.5 Research Objectives

The main part of this research was to study the preparation and characterizations of cobalt (II) doped Zn_2SiO_4. The objectives of this research are summarized as follow:

1. To synthesize the cobalt (II) doped Zn_2SiO_4 using the sol-gel method.
2. To study the effect of sintering temperature towards structural and optical properties of undoped and cobalt (II) doped Zn_2SiO_4.
3. To study the effect of cobalt (II) doping toward structural and optical properties of Zn_2SiO_4.

1.6 Scope of The Study

The scope of the study are stated as follows:

1. Cobalt (II) doped Zn_2SiO_4 was prepared using the sol-gel method. The following stoichiometric equation, $Zn_{(2-x)}Co_xSiO_4$ where x = 0, 1, 2, 3, 4 and 5 mol% of cobalt (II) concentration were applied in preparation of the sample. All starting materials were used as reference materials.
2. Sintering temperature to prepare Zn_2SiO_4:Co^{2+} nanoceramics were varied from 600 to 1000 °C.
3. The structural properties, which includes phase structure, surface morphology, chemical composition, and bonding formation were characterized using XRD, FESEM, EDX and FTIR analysis.
4. The optical studies, which includes absorption, optical band gap and luminescence intensity of the samples were measured using UV-Vis-NIR and Photoluminescence spectroscopy.

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1.7 Outline of Thesis

This thesis begins with Chapter 1, with an introduction to zinc Zn_2SiO_4 with the addition of doping ions such as transition metals and rare earth element. Previous and recent studies by other researches were reviewed in Chapter 2. In Chapter 3, methodology in preparation and characterization of the research were explained in detail. The results were highlighted and discussed including different heat treatments and compositions towards the physical, structural, and optical properties of cobalt (II) doped Zn_2SiO_4 briefly in Chapter 4. The conclusion of the study and recommendation for future works were given in Chapter 5.

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