UNIVERSITI PUTRA MALAYSIA

ROLE OF SiO2 IN THE SYNTHESIS OF Zn2SiO4 COMPOSITE ON PHYSICAL, STRUCTURAL AND OPTICAL PROPERTIES

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ITMA 2018 6

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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 Doctor of Philosophy

December 2017

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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December 2017

Chair: Khamirul Amin Bin Matori, PhD
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Zinc silicate (Zn_2SiO_4), or willemite ceramic is an attractive material and has a wide range of applications. A lot of attention has been given to the synthesizing of Zn_2SiO_4 with better properties. This involves applying a new technique, or modifying existing methods. In this study, Zn_2SiO_4 composite-based ceramic was synthesised using amorphous SiO_2 nanoparticles as a silicon source. The amorphous SiO_2 nanoparticles were obtained from a simple precipitation process of preparing aqueous sodium silicate with ethanol at different reaction times. Different ratios of Zn:Si were prepared by mixing amorphous SiO_2 nanoparticles with aqueous zinc nitrate. Amorphous SiO_2 nanoparticles were encapsulated by the zinc source in aqueous solution, dried, and subjected to heat treatment. The produced SiO_2 nanoparticles were in amorphous form according to the XRD pattern. The range of particle size was between 63.5 ± 4.0 to 99.0 ± 3.1 nm, which increased with increasing reaction time. The sample with 90 minutes of reaction time showed fine pore characteristic, with the highest total pore volume of 0.4804 cm^3g^{-1}. This characteristic had significantly changed the optical properties of the final product. The heat treatment underwent by the amorphous SiO_2 nanoparticles, with zinc source mixture, showed the changing of phases, morphology, and size with increased temperature. During calcination, ZnO phase appeared at the beginning of heat treatment and Zn_2SiO_4 phase started to emerge at 800 °C onwards, as shown by XRD patterns. This observation is supported by the FTIR spectrum, which identified SiO_2, ZnO_4, and Zn-O-Si bands that referred to the Zn_2SiO_4 phase. Optical band gap analysis of Zn_2SiO_4 composite was determined to be within the range of 3.12 ± 0.04 to 3.19 ± 0.04 eV. The photoluminescence of treated samples showed emission peaks at 411 and 455 nm wavelengths from ZnO's blue band and at 528 nm wavelength from Zn_2SiO_4's green band. The availability of zinc ions on the surface and inner pore sites of the amorphous SiO_2 nanoparticles could have diffused and formed Zn_2SiO_4 during heat treatment at much lower temperatures. The diffusion of zinc ions into Zn_2SiO_4 composite with high surface area will favour the diffusion at a much lower temperature compared to a conventional solid state method. This optical characteristic is expected to be a potential candidate for applications using phosphor materials and in opto-electronic devices.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PERANAN SiO_2 DALAM SINTESIS KOMPOSIT Zn_2SiO_4 TERHADAP SIFAT FIZIKAL, STRUKTURAL DAN OPTIKAL

Oleh

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Seramik berasaskan zink silikat (Zn_2SiO_4) atau willemite adalah salah satu bahan yang mempunyai daya tarikan dan meluas kegunaannya. Banyak perhatian telah diberikan untuk sintesis Zn_2SiO_4 bagi meningkatkan sifat-sifatnya. Ini termasuklah dengan memperkenalkan teknik baru atau pun mengubahsuai kaedah yang sedia ada. Dalam kajian ini, seramik berasaskan komposit Zn_2SiO_4 disintesis dengan menggunakan nanopartikel amorfus SiO_2 sebagai sumber silikon. Nanopartikel amorfus SiO_2 diperolehi melalui proses pemendakan ringkas sodium silikat akueus dengan etanol pada masa tindakbalas yang berbeza. Nisbah berbeza Zn:Si disediakan dengan mencampurkan nanopartikel amorfus SiO_2 dengan zink nitrat akueus. Nanopartikel amorfus SiO_2 diliputi oleh sumber ion zink dalam larutan akueus, dikeringkan dan diikuti dengan rawatan haba. Serbuk nanopartikel SiO_2 yang terhasil adalah bersifat amorfus berdasarkan kepada corak pola XRD. Julat saiz partikel adalah di antara 63.5 ± 4.0 hingga 99.0 ± 3.1 nm dan meningkat dengan dengan masa tindak balas. Sampel dengan masa tindakbalas 90 minit menunjukkan sifat poros dengan jumlah isipadu poros purata yang tinggi iaitu 0.4804 cm^3g^{-1}. Ciri-ciri ini turut memberikan kesan dalam sifat optikal kepada produk akhir. Rawatan haba bagi campuran nanopartikel amofus SiO_2 dengan sumber zink menunjukkan perubahan fasa, morfologi dan saiz dengan peningkatan suhu. Semasa pengkalsinan, fasa ZnO muncul pada permulaan rawatan haba dan fasa Zn_2SiO_4 mula terbentuk pada suhu 800 °C dan ke atas seperti yang ditunjukkan dalam corak pola XRD. Pemerhatian ini disokong dengan pengukuran FTIR yang dikenalpasti sebagai ikatan SiO_2, ZnO_4 dan Zn-O-Si yang merujuk kepada fasa Zn_2SiO_4. Analisis terhadap jurang jalur optik bagi komposit Zn_2SiO_4 telah ditentukan berada dalam julat 3.12 ± 0.04 hingga 3.19 ± 0.04 eV. Kefotopendarcahayaan bagi sampel yang terawat haba menunjukkan puncak pancaran pada panjang gelombang 411 dan 455 nm yang terhasil dari ZnO untuk jalur biru dan panjang gelombang 528 nm untuk jalur hijau Zn_2SiO_4. Ketersediaan ion zink pada permukaan dan bahagian dalam poros bagi nanopartikel amorfus SiO_2 membolehkan peresapan dan pembentukan Zn_2SiO_4 pada suhu rawatan haba yang lebih rendah. Peresapan ion zink ke dalam komposit Zn_2SiO_4 yang mempunyai luas permukaan yang tinggi akan memberikan kelebihan peresapan pada suhu yang lebih

rendah berbanding dengan kaedah keadaan pepejal konvensional. Ciri-ciri optik ini dijangka berpotensi untuk diaplikasi dalam bahan fosfor dan peranti opto-elektronik.

ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious and the Most Merciful. I am very grateful to Allah for the blessing to be able to complete my thesis.

Thanks to my supervisor, Associate Prof. Dr. Khamirul Amin Matori, for his supervision and constant support. His invaluable help of constructive comments and suggestions throughout the experimental and thesis works have contributed to the success of this research.

Furthermore, my appreciation to the committee members Prof. Dr. Sidek Hj. Abd Aziz and Prof. Dr. Elias Saion for the support and guidance regarding this topic. My appreciation also goes to all the staff and technicians of the Institute Advanced Technology and Faculty of Science, Universiti Putra Malaysia for the co-operation and technical support provided. Sincere thanks to all members of Glass, Ceramic, Composite and Metal Laboratory for their help and moral supports upon the completion of my project.

Last but not least, my deepest gratitude goes to my parents and my wife and families for their endless love, prayers and encouragement.

May Allah bless all of the people for giving me the utmost support in completion of my study.

I certify that a Thesis Examination Committee has met on 18 December 2017 to conduct the final examination of Engku Abd Ghapur bin Che Engku Ali on his thesis entitled "Role of SiO_2 in the Synthesis of Zn_2SiO_4 Composite on Physical, Structural and Optical Properties" 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 Doctor of Philosophy.

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This is to confirm that:

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LIST OF ABBREVIATIONS AND SYMBOLS

Zn_2SiO_4	Willemite/zinc silicate
$Zn_2SiO_4:Mn^{2+}$	Willemite-doped manganese
$(Zn(NO_3)_2$	Zinc nitrate
$Zn(CH_3COO)_2$	Zinc acetate
SLS	Soda lime silica
SiO_2	Silica oxide
ZnO	Zinc oxide
MnO	Manganese oxide
CaO	Calcium oxide
Na_2O	Sodium oxide
Al_2O_3	Aluminium oxide
$MnCO_3$	Manganese carbonate
$ZnCl_2$	Zinc chloride
Na_2SiO_3	Sodium silicate
$MnCl_2$	Manganese(II) chloride
α	Alpha
β	Beta
γ	Gamma
PVA	Polyvinyl alcohol
PZC	Point of zero charge
IEP	Isoelectric Point
r.f.	radio frequency
MSN	mesoporous silica nanoparticles
XRD	X-ray diffraction
TEM	Transmission electron microscopy
FESEM	Field emission scanning electron microscopy
FTIR	Fourier-transform infrared
TEOS	Tetraethyl orthosilicate
CTAB	Cetyltrimethylammonium bromide
SDS	Sodium dodecyl sulfonate
PEG	Polyethylene glycol
PL	Photoluminescence
HCl	Hydrochloric acid
CRT	Cathode ray tube
N_2	Nitrogen gas
Ar_2	Argon gas
CO	Carbon monoxide
NH_2	Ammonia
H_2SiO_3	Silicic acid
HNO_3	Nitric acid
NH_4OH	Ammonia
µm	Micrometre
nm	Nanometre
eV	Electron volt
JCPDS	Joint Committee on Powder Diffraction Standards

CHAPTER 1

INTRODUCTION

1.1 Research background

Oxide-based phosphors have received a great deal of interest since the development of electronic displays and other applications. Phosphors are used as a light source in display devices, detector systems, such as X-ray screens and scintillators, and for luminous paint, or coating. The increasing demand for phosphor is due to its ability to replace the conventional incandescent lamps and fluorescent lamps for lighting. High energy consumption is needed to heat the high-temperature tungsten filament lamps and mercury vapour discharge lamps. With new high technology display devices, such as plasma displays, field emission display, electroluminescence display, and vacuum fluorescent display, the demand for better performance phosphor materials will never end (Ye et al., 2010; Yen et al., 2007).

Continuous research are being conducted to improve the properties of phosphor materials associated with the enhancement of stability, simplified synthesis methods, and controlling the functional properties of materials. Among the numerous inorganic phosphors, Zn_2SiO_4-based materials are widely used in the industry because of their physical and chemical stabilities (Takesue et al., 2009).

Traditionally, Zn_2SiO_4 is prepared using a solid state reaction method by applying heat treatment to a mixture of zinc oxide (ZnO) and silica (SiO_2) as the precursors. Other starting materials have also been used. The physical, chemical, and optical properties of the resulting Zn_2SiO_4 depend on the preparation method and starting materials. As for silicate-based phosphor, the selection of silica precursors can certainly influence the final properties of the targeted materials. Conventionally, ZnO and SiO_2 powder-type precursors are used with appropriate stoichiometry and heated at a high temperature to form Zn_2SiO_4.

Apart from the laboratory grade SiO_2, soda lime silica produced from waste materials (Samsudin et al., 2016; Zaid et al., 2016a), silicon alkoxide, or tetraethyl orthosilicate (TEOS) (Lu et al., 2011), and commercialized mesoporous SiO_2 (Li et al., 2013) are among common SiO_2 sources. The conventional melt quenching of soda lime silica, mixed with ZnO, produces a glass precursor, which is then subjected to heat treatment to form Zn_2SiO_4-based glass-ceramic. The drawback of using soda lime silica is the presence of other elements in the glass, which can affect the properties of the final materials (Zaid et al., 2012). TEOS is a liquid SiO_2 precursor that needs to be added into a mixture of water and alcohol solvent for the Si ions to react with zinc ions. A suitable ratio of water to alcohol solvent is required for the hydrolysis of TEOS to occur and to form Zn_2SiO_4. Consequently, the hydrophobic properties (Zeng et al., 2009) and toxicity

of TEOS (Nakashima, 1994) become drawbacks to those that have specific requirements during production.

The sol-gel method to produce SiO_2 is mostly related to alkoxide-based chemistry. Recently, silicate-based processes were re-investigated in the context of green sol-gel chemistry, which were focused on non-toxic aqueous precursors, with low environmental impacts that can be used under solvent-free conditions (Baccile et al., 2009). Another suitable candidate is sodium silicate, or water glass. Sodium silicates are obtained from the fusion of silica sources, mainly from nature, such as silica sand, or silica ash from plants, with soda ash, or sodium hydroxide that is dissolved in water. They constitute as the starting products for the synthesis of colloidal silica by acidification, either via sulphuric acid addition, or via an ion exchange resin (Elimelech and Avnir, 2008; Wu et al., 2012; Sundblom et al., 2011).

SiO_2 particles with different morphologies can be obtained by controlling the process parameters. Amorphous spherical SiO_2, with a size in the range of several micrometres, can be obtained using the sol-gel method (Godoi et al., 1999). The production of porous silica from water glass has been reported using anionic or cationic surfactants, or capping agents, such as cetyltrimethylammonium bromide (CTAB) (Yun-yu et al., 2012), sodium dodecyl sulfonate (SDS) (Cheng and Liu, 2003), and polyethylene glycol (PEG) (Elimelech and Avnir, 2008), to control the size and porosity.

Although surfactants can lead to better properties, their usage could increase the production cost. With a simple route of reaction, porous silica powder can be synthesised from the reaction of water glass with weak acids, such as alcohol (ethanol), as demonstrated by Buining et al. (1996) and Godoi et al. (1999). The resulting porous silica particles can offer an advantage when used as a precursor during the formation of the Zn_2SiO_4 phase. Porous silica made of water glass has different porosity characteristics due to the reaction with a weak acid.

In place of ZnO solid powder, water soluble zinc precursors can also be used as zinc ion sources. Known as an environmentally friendly material, the selection of a less hazardous soluble zinc source is equally important as the SiO_2 source. The salt of amphoteric zinc oxide, with nitric acid or a weak acid, such as acetic acid, have been recognized as zinc nitrate and zinc acetate. Water solubility is another key point for mixing zinc ions with the source of SiO_2 (Bahadur et al., 2007; Singh et al., 2009). ZnO has a band gap of ~3.3 eV and shows the emission in the visible range, namely, the blue, green, and red regions because of the defects present with its structure (Foo et al., 2014).

The small sized ZnO, with its wide band gap (5.5 eV) that made up Zn_2SiO_4 offers a unique optical property to this composite material. Doped Zn_2SiO_4 composite has been identified as having the ability to tune the emission of colour coordinates and correlate colour temperature for optical display (Ramakrishna et al., 2014). Zn_2SiO_4, or also known as its mineral name, willemite, has been recognized as one of the host matrices for phosphor materials. Zn_2SiO_4 has been established as having physical and chemical stabilities, and the advantages of luminescence. Mn^{2+}-doped zinc silicate has been

extensively used as a green luminescence phosphor in opto-electronic devices. The doping of Mn^{2+} gives the green and red emissions due to the d–d electronic transition ($^4T_1(4G) \rightarrow {}^6A_1(6S)$ of Mn^{2+}) (Popovich et al., 1993; Cho and Chang, 2003; Mbule et al., 2016). Doping Zn_2SiO_4 with other elements, such as transition metals, or rare earth elements are studied to increase the performance of the phosphor. Nonetheless, limited reports have discussed the effect of ZnO phase when it coexists with Zn_2SiO_4 phase to form a composite.

With the aim of improving material properties as well as the processing temperature and time, many wet chemical methods have been proposed, such as sol-gel method, hydrothermal method, and combustion, or thermal pyrolysis method. Sol-gel method is performed by mixing a zinc ion source (such as sulphate, acetate, and nitrate) and a silicon ion source (such as alkoxysilanes and sodium silicates) in a solvent to produce a uniform solution, which is followed by drying. Most of the resulting dried compounds are amorphous and have to be calcined at high temperatures to obtain crystalline α-Zn_2SiO_4 phase (Lin and Shen,1994; Zhang et al., 2003; Petrovykh et al., 2015; El Ghoul and El Mir, 2014).

Comparatively, mesoporous SiO_2 nanoparticles have been used as a base material and dissolved zinc ions are incorporated through impregnation into SiO_2 pores, mostly in aqueous conditions (Taghavinia et al., 2001; Cannas et al., 2003). The chemically reactive surface of both SiO_2 and ZnO during mixing is suggested as one of the factors that can contribute to reduce phase formation temperature (Yao et al., 2000; Lihitkar et al., 2012). In addition, the high surface area of the silica source could also influence the final properties of Zn_2SiO_4 composites (Gun'Ko et al., 2013; Ramakrishna et al., 2014).

In the current study, the source of amorphous silica nanoparticles was sodium silicate (Na_2SiO_3) from a simple precipitation method using ethanol in deionized water. The physical, chemical, and structural properties of the amorphous silica nanoparticles have been characterized to study the effect of different reaction times during the synthesis. The Zn_2SiO_4 composites were prepared by impregnating water soluble zinc nitrate hexahydrate with amorphous silica in de-ionized water. The physical, structural, and optical properties of the heat treated samples were analysed using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared (FTIR), Uv-Visible (Uv-Vis), thermal analysis, and photoluminescence (PL) spectroscopy. The aim of this work is to study the role of SiO_2 in the synthesis of Zn_2SiO_4 as a potential material to be used in the opto-electronic field as a phosphor material.

1.2 Problem statement

In recent years, interest on the synthesis and analysis of Zn_2SiO_4 composite has grown due to its potential in optical and lighting devices. Previous studies have focused on improving synthesis methods, and using low cost, less hazardous precursor materials. In this study, the wet chemical impregnation method, combined with sintering, was used to synthesise Zn_2SiO_4 composite. This technique provided a simple preparation route that

did not require special equipment during synthesis (Taghavinia et al., 2001). In this method, solid SiO_2 particles were used as a template and mixed with a solvent containing dissolved zinc ions from zinc nitrate hexahydrate. To gain better interactions between SiO_2 and zinc ions, amorphous SiO_2 nanoparticles were synthesised as a template.

A simple precipitation method was applied to synthesise amorphous SiO_2. The amorphous SiO_2 nanoparticles were synthesised from sodium silicate, also known as water glass that is competitive in cost (Zulfiqar et al., 2016). Chemically synthesised SiO_2 has an advantage due to the ability to control the process parameters. Apart from the nanosize particles that have drawn great attention because of their high surface areas, the porous structure of the produced nanoparticles could also influence the properties of the resulting particles.

The formation of the final product solely depends on the heat treatment of SiO_2 and zinc nitrate mixture. The zinc ions deposited onto the surface of silica nanoparticles provide ample reaction interface between both elements to form a new phase. Although heat treatment temperature is seen as the main driver for reaction to occur, the properties of amorphous SiO_2 nanoparticles and the ratio between silicon and zinc ions should also be taken into account (Lu et al., 2011). This mixture formed the main crystal phase of Zn_2SiO_4 after heat treatment. The formation of Zn_2SiO_4 composite offers some information on the physical properties of the final product. Furthermore, the applications of composite-based phosphor due to the broad range of colours can be achieved by doping it with various elements. This type of phosphor is usually applied as a lighting source and in display panels.

Therefore, the synthesised amorphous SiO_2 nanoparticles and their role in the synthesis of Zn_2SiO_4 composite were studied. The physical, structural, and optical properties of Zn_2SiO_4 composite were expected to offer important information for its application as a potential phosphor material in optoelectronic devices.

1.3 Objectives of study

The objectives of this study are summarized as follows:

1) To synthesise amorphous SiO_2 nanoparticles using a simple precipitation method.
2) To synthesise Zn_2SiO_4 composites using a wet chemical (wet impregnation) method, with amorphous SiO_2 nanoparticles as the template.
3) To study the effects of sintering temperature and Zn:Si ratio towards the physical, structural, and optical properties of Zn_2SiO_4 composites.
4) To relate the morphological and physical properties of amorphous SiO_2 nanoparticles to the physical, structural, and optical properties of Zn_2SiO_4 composites.

1.4 Scope of study

The scopes of the study are:

1) Amorphous silica nanoparticles were prepared using aqueous sodium silicate in de-ionized water at different reaction times of 30, 60, 90, 120, and 180 minutes using a simple precipitation method.
2) The dried amorphous silica nanopowder was mixed with aqueous zinc nitrate, with the ratio of zinc to silica of 2:1, 1.75:1, 1.5:1, and 1.25:1. Then, the mixture was dried in a petri dish for 24 hours at 120 °C.
3) The dried powder was then sintered from 600 °C to 1000 °C for approximately 3 hours.
4) The physical, structural, and optical properties of the amorphous SiO_2 nanoparticles and Zn_2SiO_4 composites were characterized using XRD, FESEM, TEM, FT-IR, nitrogen gas adsorption and desorption technique, Raman spectroscopy, UV-Vis, and PL spectroscopy.

1.5 Importance of study

Recently, Zn_2SiO_4 received considerable attention as a candidate for opto-electronic application to replace the historical use of the green display panel in the cathode ray tube. Subsequently, the growing number of applications has increased the demand for better performance phosphor. The requirements of current devices to be mobile, compact, and with high quality display are from device developers. Despite the rapid development in device technology, the element of green technology, cost-effectiveness, and simplicity in the synthesizing processes are also taken into consideration. Under these circumstances, the synthesising method and precursor materials for this study were specifically chosen to study those factors.

This study was focused on synthesising Zn_2SiO_4 composite using a wet impregnation method. This method applied amorphous silica nanoparticles as a morphology-controlling template to perform chemical reactions or for new phase formation when combined with other ions; in this case, zinc ions. It was expected that the properties of Zn_2SiO_4 composite, based on the amorphous silica nanoparticles synthesised using the wet impregnation method, could contribute as new knowledge to synthesise phosphor materials.

1.6 Outline of thesis

The overall thesis consists of five chapters, including this introductory chapter. Chapter Two begins by laying out the details about the materials involved in this work, and the previous and current trends of research for SiO_2 and Zn_2SiO_4 composites. The third chapter is concerned with the methodology used in this study. The fourth chapter presents the findings, focusing on the properties of amorphous silica nanoparticles, the effect of using synthesised amorphous silica nanoparticles, and the effect of sintering temperature to form Zn_2SiO_4 composite. The final chapter will conclude the findings and offer suggestions for future works.

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