UNIVERSITI PUTRA MALAYSIA

EFFECTS OF CALCINATION TEMPERATURES ON STRUCTURAL AND OPTICAL PROPERTIES OF ZINC OXIDE, SILICON DIOXIDE AND WILLEMITE SYNTHESIZED BY SIMPLE THERMAL TREATMENT

ALIBE IBRAHIM MUSTAPHA

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By

ALIBE IBRAHIM MUSTAPHA

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

January 2016

DEDICATION

This thesis solely dedicated to my Beloved Dad and Mum, Hon Mustapha Ali Benshiekh and Zara Kellu Alibe

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Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree Master of Science.

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January 2016

Chairman : Associate Professor Khamirul Amin Matori, PhD
Institute : Institute of Advance Technology

Phosphor host materials are subjects of continuing study in materials sciences because their physical and chemical properties and wide range of applications. Several methods and techniques have been applied for the synthesis of phosphor host materials. Most of these techniques are difficult to employ in a larger scale production due to the complicated procedures, longer reaction period, high reaction temperatures involved, toxic reagents and by–products which are potentially harmful and unfriendly to the environment. In this study, the Zinc oxide (ZnO), Silicon dioxide (SiO_2) and Willemite were successfully synthesized using simple thermal treatment method from an aqueous solution containing only zinc acetate and silicon tetraacetate, poly(vinyl pyrrolidone), and deionized water. The characterization studies of the nanoparticles formed were carried out by Thermogravimetry analysis (TGA), X–ray Diffraction spectroscopy (XRD), Electron Dispersive X–ray spectroscopy (EDX), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FT–IR), UV–Vis Spectrometer and PL Spectroscopy. The corresponding peaks of Zn, Si and O were observed in the EDX analysis of the sample which reveals their presence in $ZnSiO_4$, while in the preparation of SiO_2 the only peak of Si and O were observed. The Zn and O peaks in the EDX spectra ZnO reveals their presence. The XRD patterns confirmed the formation of nanoparticles of ZnO and Zn_2SiO_4 NPs. the XRD confirms that the SiO_2 formed were in the amorphous state as there was no peak exhibited. The results from the FESEM and TEM shows that the particle size increased with the calcination temperature increased from 23.8 to 37.7 nm between 500 –750 °C in the case of ZnO, and the willemite phase formed at 1000 °C had 43.7 nm crystal size. The SiO_2 particles calcined at 500–750 °C were <10 nm from the TEM images. The FT–IR spectra show only the principle absorption bands of Si–O–Si and Zn–O located at wavenumber less 1000 cm^{-1} respectively confirms the formation of ZnO, SiO_2 and Zn_2SiO_4 NPs. The ZnO band gap energy was determined from UV–vis reflectance spectra using the Kubelka–Munk function and the band gaps were found to decrease with increase in calcination temperature due to particle size increased from 3.325–3.245 eV calcined from 500–750 °C. The absorbance spectra were used to determine

the band gap energy of SiO_2 and Zn_2SiO_4. The wide band gap of 3.123– 4.352 eV for SiO_2 samples calcine between from 500–750 °C was recorded. Willemite phase formed at 800, 900 and 1000 °C possessed a wide band gap of 5.460, 5.527 and 5.527 eV respectively. The PL analysis of ZnO NPs when excited at 300 nm reveals the various deep level defect originated from zinc interstitial while the PL analysis of $Zn2SiO_4$ NPs at higher calcination temperature reveals deep level defects in the blue region related to oxygen vacancies often referred to as blue emission. The blue band observed for all samples in the PL analysis of SiO_2 NPs have been believed to have originated from electron hole recombination of self–trapped exciton.

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

KESAN RAWATAN HABA TERHADAP STRUKTUR DAN SIFAT OPTIK BAGI ZINK OKSIDA, SILICA DIOKSIDA DAN WILLEMITE, YANG DISINTESIS DENGAN KAEDAH RAWATAN HABA RINGKAS

Oleh

ALIBE IBRAHIM MUSTAPHA

Januari 2016

Pengerusi : Professor Madya Kamirul Amin B Matori, PhD
Institut : Institut Teknologi Maju

Bahan perumah fosfor adalah subjek kajian yang berterusan dalam bidang sains bahan kerana sifat fizikal dan kimia mereka mempunyai pelbagai aplikasi. Beberapa kaedah dan teknik telah digunakan bagi hos sintesis. Kebanyakkan teknik ini sukar untuk digunakan dalam penghasilan skala yang lebih besar disebabkan oleh prosedur yang rumit, masa tindak balas yang lebih lama, melibatkan suhu tindak balas yang tinggi, reagen toksik dan produk sampingan yang mempunyai potensi yang berbahaya, dan tidak mesra kepada alam sekitar. Dalam kajian ini, oksida zink (ZnO), silikon dioksida (SiO_2) dan Willemite telah berjaya disintesis melalui kaedah rawatan haba dari larutan akueus yang mengandungi hanya zink asetat dan silikon tetraacetate, poli (vinil pyrrolidone), dan air ternyahion. Kajian pencirian bagi zarah nano yang dihasilkan telah dijalankan dengan analisis termogravimetri (TGA), spektra belauan sinar–X (XRD), spektra serakan electron sinar–X (EDX), Transmisi Mikroskop Elektron (TEM), Fourier Transform Infrared Spektroskopi (FT–IR), UV–Vis Spektrometer dan PL Spektroskopi. Puncak sepadan bagi Zn, Si dan O telah diperhatikan dalam analisis EDX sampel yang menunjukkan kewujudan Zn_2SiO_4, manakala dalam penyediaan SiO_2 hanya puncak Si dan O telah dikesan. Pada spektrum EDX ZnO menunjukkan terpatpuncak Zn dan O. Corak spektrum XRD mengesahkan pembentukan ZnO dan Zn_2SiO_4 berzarah nano. XRD mengesahkan bahawa SiO_2 terbentuk dalam keadaan amorfus kerana tiada puncak dapat dikesan. Keputusan dari XRD, FESEM dan TEM menunjukkan bahawa saiz zarah akan meningkat dengan peningkatan suhu pengkalsinan daripada 23.8 nm kepada 37.7 nm bagi suhu 500 –750 °C bagi ZnO, dan fasa willemite dicerap pada suhu 1000 °C dan mempunyai saiz hablur 43.7 nm. Zarah SiO_2 terkalsin antara 500–750 ° C adalah <10 nm dari imej–imej TEM. Spektrum FT–IR menunjukkan hanya jalur penyerapan utama bagi Si–O–Si dan Zn–O yang masing–masing terletak di nombor gelombang kurang 1000 cm–1 mengesahkan pembentukan ZnO, SiO_2 dan Zn_2SiO_4. Jalur jurang tenaga bagi ZnO telah ditentukan daripada UV–vis spektrum pantulan menggunakan kaedah Kubelka–Munk dan jurang band didapati berkurangan dengan peningkatan suhu pengkalsinan disebabkan oleh peningkatan saiz zarah dari 3.325–3.245 eV selepas dikalsinkan pada suhu 500–750 °C. Teknik spektrum penyerapan juga telah digunakan untuk menentukan tenaga jurang jalur bagi SiO_2 dan Zn_2SiO_4. Jurang jalur

dengan luas 3.1237–4.3522 eV untuk SiO_2 telah direkodkan selepas dikalsinkan pada suhu 500–750 °C. Fasa Willemite terbentuk pada suhu 800, 900 dan 1000 °C dan memiliki jurang jalur yang luas iaitu masing–masing dengan 5.460, 5.527 dan 5.527 eV. Analisis PL ZnO NP apabila teruja pada 300nm mendedahkan pelbagai kecacatan peringkat mendalam berasal dari celahan zink manakala analisis PL bagi Zn_2SiO_4 NP pada suhu pengkalsinan yang lebih tinggi mendedahkan kecacatan tahap mendalam di dalam kawasan biru yang berkaitan dengan kekosongan oksigen yang sering dirujuk sebagai pelepasan biru. Jalur biru dilihat pada semua sampel dalam analisis PL bagi SiO_2 NP telah dipercayai berasal dari penggabungan semula elektron–lubang daripada terperangkap–diri exciton.

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All thanks and praises be to The All–Mighty Allah, the Most Beneficent and the Most Merciful by whose power I accomplished this challenging task.

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I certify that a Thesis Examination Committee has met on 19 January 2016 to conduct the final examination of Alibe Ibrahim Mustapha on his thesis entitled "Effects of Calcination Temperatures on Structural and Optical Properties of Zinc Oxide, Silicon Dioxide and Willemite Synthesized by Simple Thermal Treatment" 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.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree Master of Science. The members of the Supervisory Committee were as follows:

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Declaration by graduate student

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Declaration by Members of Supervisory Committee

This is to confirm that:

- The research conducted and the writing of this thesis was under our supervision;
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Signature: ____________________________
Name of Member of Supervisory Committee: Elias Saion PhD

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LIST OF SYMBOLS

°C	Degree
A	Lattice parameter
Cm	Centimeter
D	Crystal size
eV	Electron Volt
F	Frequency
G	Gram(s)
H	Hour(s)
KM	Kubelka–Munk
M	Meter
Mg	Milligram
Min	Minute(s)
Mmol	Millimole
Mn	Manganese
Nm	Nanometre
O_2	Oxygen
Si	Silicon
Zn	Zinc

LIST OF ABBREVIATIONS

DCCAs	Drying control chemical additives
FESEM	Field electron scanning microscopy
FT–IR	Fourier transforms infrared
HCl	Hydrochloric acid
KM	Kubelka–Munk
LPG	Liquid petrol gas
NPs	Nanoparticles
PEG	Polyethylene glycol
PL	Photoluminescent
PVP	Poly(vinyl pyrrolidone),
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UV–vis	Ultraviolet–visible spectroscopy
XRD	X–ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

In December 1959, a famous lecturer named R. Feynman, a professor at California Institute of Technology delivered a speech at a conference of American physical society that was titled “There is plenty of room at the bottom”. For the first time the idea of “NANO” was mentioned in the event, and he made some remarks “I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle”. Feynman elaborated much on the numerous technical application of the field (Feynman, 1960).

In 1974, Tsnoguchi from Tokyo Science University gave a definition of nanotechnology as “Consist of the processing of separation, consolidation, and deformation of material by one atom or by one molecule” (Taniguchi, 1974). A quite number of significant discoveries and invention was made while in the second half of the 1980s to early 1990s which develop an essential impact on the further development of the nanotechnology. After that, nanotechnological research and design were intensified; its practical application expands, and a considerable number of organization and countries got involved in it. In the past decades, most of the scientist and researchers have agreed upon the idea of nanotechnology deals with the broad field of applied science and technologies in design, fabrication, characterization of the nanoscale material (typically ranging from 1–100 nm), and the assembly of nanoscale devices. In general concept, a material can be referred to as “nano–structured” if they have at least one dimension that is less than 100 nm, for instance, filamentary structures, atomic clusters, layered films and bulk nanostructured materials.

Nanoscience and nanotechnology are two themes in the study of nanomaterials (Bandaru et al., 2005). Nanoscience is more related to definition of fundamentals of nanomaterial which consist of the both experimental and theoretical aspect, synthesis and features of nanomaterial (Krusin–Elbaum et al., 2004). While nanotechnology is the general term used in the technology and engineering part involved in the manipulation of matter that include the development, application and implication material in nanoscale.

Nanotechnology is multi–disciplinary specialization which cut across the conventional boundaries between physics, chemistry, mathematics, biology and engineering (Salata, 2004). Using these concepts the technologist and engineer maneuver materials at nanoscale to create a product which make use of remarkable features.

In nanomaterial research and development, synthesis and characterization plays an important role. Top–down and bottom–up approach technique, are the two major approaches for nanomaterials assembling. In top–down method, nanomaterials are constructed from large size material without molecule level control (Wong et al., 2009). While the bottom–up approach is where materials are constructed from a few molecule components by chemical self–assembling in solution into functional superstructures (Wong et al., 2009). Due to simplicity, and a short period of processing, top–down approach is mostly applied in industries.

Nanomaterials have attracted considerable attention from researchers around the world in recent years, due to the "quantum size effect" phenomenon: The properties of a material such as physical, chemical, electrical and optical properties while in nano–scale differs a lot from those bulk size. Usually, the elemental composition and crystal structure of a bulk size material determines most of its chemical and physical properties. Surface atom in bulk material plays a negligible role in most of its properties because it only accounts for a little fraction of total atoms. While in nano–scale since the particle size has decreased, the surface atom tends for a greater proportion of the total, hence are no longer negligible. It is always important to note that either in bulk or nano–scale materials, the activity between the external media and surface atoms, under certain given conditions, can dramatically affect reactions such as crystal growth and catalysis on either bulk or nano–scale materials. Figure 1 gives the illustration that surface atom proportion increases significantly as the particle size was smaller than 20 nm.

A new physical and chemical property emerges due the dramatic increase in a surface atom in the total; such include optical, catalytic ability and a change of magnetization. The dramatic increase of surface atom percentage in total atoms leads to the appearance of new chemical and physical properties of nanoparticles such as the emergence of catalytic ability, featured optical spectra, and a change of magnetization.

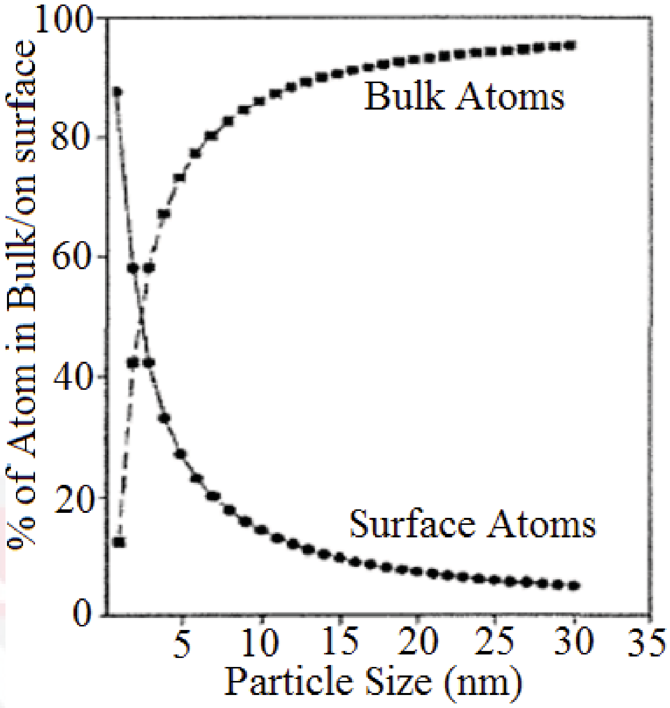

Figure 1.1 The percentage of atoms in bulk and on the surface as a function of particle size (Fuller et al., 2002).

The Greater surface area tends to expose more atoms to the external environment, which changes both physical properties and chemical properties of nanoparticles. Surface chemistry is vital in the areas of corrosion, catalysis, and absorption. Most often chemical reactions take place at the interface between two phases, larger area of interface raises more chances of contact between the reactants, which results in more active interactions. Thus many reactions, which cannot take place in bulk–sized materials, can now occur in nano–sized materials.

Summarily, Nanoparticles (NPs) tends to be more reactive and sensitive to the outer environment when the surface area or surface atom is increased, this will render it a potential application and a market value which cannot be obtained in the bulk material. These applications are promising in a wide range of human endeavors such as pharmaceutical industries disease detection and control, genetic study, optical devices, solar cells, batteries, catalysts, and sensor. Moreover, during past decade, different specializations have begun to work with one another to pave a way to advanced technologies and cutting–edge instruments for advancing nanotechnology. The main driving force behind the explosion in nanomaterials research interest is attributed to the unusual physical and chemical properties and yet the huge applications.

1.2 Phosphor and Phosphor host material

Phosphors also refer to a luminescent material, are those materials that exhibit the phenomenon of luminescence which they can emit light after being exposed to radiation such as ultraviolet light or electron beam. The phosphor material is useful in a variety of display applications like electroluminescent, photo luminescent, cathode ray tubes (CRTs), X–ray detectors, LEDs and LCDs (Birkel et al., 2012; Chen et al., 2010).

Phosphor host is usually an inorganic material with a large band gap that could be an oxide, silicate, nitride, oxynitride, halide, oxyhalide, selenide, or sulfide which is transparent to the incident radiation (George et al., 2013; Xie and Hirosaki, 2007).

1.3 Problem Statements

Phosphor industries have been condemned for the high energy they consumed and carbon emission due the high temperature of annealing involved (Zhang and Cheng, 2009; Canadell and Raupach, 2008). In this regard, a method that involved low preparation temperature is considered to be favorable in order to mitigate energy consumption and carbon emission. However, zinc oxide (ZnO), silicon oxide (SiO_2), and willemite (Zn_2SiO_4) NPs have previously been synthesized using various methods which include a sol–gel method, ball milling method, mechanical method, chemical method, microwave method, combustion method, hydrothermal method and spray pyrolysis method. Nevertheless, most of these methods are difficult to apply on a larger scale of production owing the high temperature involve, complex procedure, longer time for the reaction to take place, toxic reagents and a harmful by–product which are not friendly to the environments. In order to give the remedy and curb the setback of the previous methods of synthesis, this study has introduced a simple thermal treatment method for synthesis zinc oxide, silicon oxide and willemite nanoparticles. The study investigates the influence of the calcination temperature on the formation of these nanoparticles by thermal treatment method and by followed the characterization of physical properties.

1.4 Significance of the study

Phosphor host materials such zinc oxide, silicon dioxide and willemite have continuously attracted scientific interest and so many investigations has been going due to their physical–chemical properties and the wide application range of optoelectronics, cathode ray tubes (CRTs) and X–ray detectors, considering such tremendous applications of these NPs in present day activities. In this study, NPs of ZnO, SiO_2 and Zn_2SiO_4 have been synthesized by thermal treatment method from an aqueous solution of zinc acetate dihydrate, silicon tetraacetate, PVP (polyvinyl pyrrolidone), and deionized water as stated earlier. The solution was dried at 80 °C for 24 h in an electric oven. The solid crystal was crush and ground before calculations at different temperature

1.5 Research Objective

The aim of the study was to synthesize, ZnO, SiO_2 and Zn_2SiO_4 NPs by simple thermal treatment method, followed by characterization of the physical properties. The objectives of the study are list below.

(i) To synthesize NPs of ZnO, SiO_2, and Zn_2SiO_4 by simple thermal treatment method.
(ii) To determine the effect of calcination temperature on the formation of such nanoparticles.
(iii) To study the effect of calcination temperature on the structural and optical properties of such nanoparticles.

1.6 Thesis outline

Synthesis and characterization of ZnO, SiO_2 and Zn_2SiO_4 NPs by simple thermal treatment method are the main feature of evaluation in this thesis. Summary of the evolution of nanoscience and nanotechnology in addition to the problem statement, the significance of the study and study objectives were stated all in Chapter one. A brief discussion on the general background of ZnO, SiO_2 and Zn_2SiO_4 NPs and common preparation and synthesis methods were discussed in Chapter 2. While in Chapter 3, the detailed clarification of the methodology and procedures involved in the synthesis of ZnO, SiO_2 and Zn_2SiO_4 NPs by thermal treatment are discussed in details. The results and discussion for characterization measurement; the thermogravimetry analysis (TGA), X–ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), Field emission scanning microscopy (FESEM), Ultra Violet visible spectroscopy (UV–vis.) and Photoluminescence measurement were explained in Chapter 4. Finally, the summary and conclusions of this research work with some recommendations for future research were given in Chapter 5. The last part of the thesis consists of the list of references, a list of publications and conferences by the author.

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