UNIVERSITI PUTRA MALAYSIA

EFFECT OF ZnO/B_2O_3 AND ZnO/SiO_2 RATIO ON PHYSICAL, STRUCTURAL AND OPTICAL PROPERTIES OF WILLEMITE-BASED GLASS CERAMIC FROM WASTE RICE HUSK

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By

AISYAH ZAKIAH KHIREL AZMAN

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

November 2019

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DEDICATION

To my mother, brothers, sister in laws and little sister for all the support and encouragements throughout my Master's studies. They supported me a lot, giving ultimate encouragements and love during my ups and down and made it possible for me to finish my Master's degree.

To my late father for whom I have been missed all these years. His unconditional love will always be remembered.

To my husband who always there through the difficulties in my studies and never fail to encourage and cheer me up. He always give advices and support whenever I need one

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Fabrication of zinc silicate with low cost material for optoelectronic industry has been attract interest amongst researchers. Therefore, in this research, zinc silicate glass-ceramic were synthesized from ZnO, B_2O_3 and waste rice husk as substitute for SiO_2 by using conventional solid-state method. In this project, a series of zinc silicate glass with empirical formula of 55-x(ZnO)x(B_2O_3)45(WRHA) where x = 5, 10 and 15 wt.% fabricated as series 1. Meanwhile, 85-y(ZnO)y(WRHA)15(B_2O_3) where y = 25, 30, 35 and 45 wt.% fabricated as series 2. Then, the effect of controlled heat treatment from 650 °C to 800 °C on the physical, structural, morphologies, phases and optical properties were measured by using Digital Electronic Density Meter, XRD, FTIR spectroscopy, FESEM, UV-Vis and PL spectroscopy. Physical investigation using digital electronic density meter shown that the density is increased with temperature and dropped at temperature above 750 °C probably because of ZnO depletion in the sample. Structural analysis with XRD shows β-willemite phase started to occur at 700 °C and with heat treatment at 750 and 800 °C, α-willemite phase can be observed. Diffraction intensity increased with heat treatment temperature. FESEM analysis revealed that with heat treatment at 650 °C, the glassy phase improved. Heat treatment above 700 °C, it shows necking appeared and above 750 °C and at 800 °C the densification increased, the surface become smoother. FTIR spectra showed the presence of ZnO_4, SiO_4 and Zn_2SiO_4 bonds which proved the formation of zinc silicate network. The effect of heat treatment temperature showed the intensity of FTIR spectra increased which is due to the bonds become stronger. Moreover, the UV-Vis analysis to investigate willemite glass-ceramic revealed the samples' optical band gap. The absorption edge shifted from shorter wavelength to longer wavelength with increase in temperature. Shifting process is due to formation of willemite in the sample. Meanwhile, the optical band gap showed decrement with increment of heat treatment temperature. Willemite crystal presence in the sample lead to scattering of the short wavelength light. The transition of optical band gap obtained is $n = 3/2$. Therefore, this ternary glass system are able to promote as a potential phosphor material for electronic devices.

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

KESAN NISBAH ZnO/B_2O_3 DAN ZnO/SiO_2TERHADAP SIFAT FIZIKAL, STRUKTUR DAN OPTIK KACA SERAMIK BERASASKAN WILLEMITE DARIPADA SEKAM PADI

Oleh

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Pengerusi : Khamirul Amin Matori, PhD
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Penghasilan zink silika menggunakan bahan kurang kos untuk industri optolektronik sudah menjadi satu tarikan dalam kalangan penyelidik. Maka, di dalam kajian ini kaca-seramik zink silika disintesis daripada ZnO, B_2O_3 dan sekam padi sebagai pengganti SiO_2 menggunakan kaedah keadaan pepejal konvensional. Di dalam projek ini, kaca zink silika dengan formula empirik $(ZnO)_{55-x}(B_2O_3)_x(WRHA)_{45}$ di mana x = 0, 5, 10 and 15 wt.% dihasilkan sebagai siri satu. Manakala, $(ZnO)_{85-y}(WRHA)_y(B_2O_3)_{15}$ di mana y = 25, 30, 35 and 45 wt.% dihasilkan sebagai siri kedua. Kemudian, kesan rawatan haba terkawal daripada 650 °C kepada 800 °C terhadap ciri-ciri fizikal, struktur, morfologi, fasa dan optik diukur menggunakan Pengukur Ketumpatan Digital, XRD, FTIR, FESEM, UV-Vis dan PL spektroskopi. Kajian percirian fizikal menggunakan densimeter menunjukkan bahawa ketumpatan bertambah dengan suhu dan jatuh pada suhu lebih daripada 750 °C disebabkan oleh pengurangan ZnO di dalam sampel. Analisis struktur menggunakan spektroskopi XRD membuktikan kehadiran fasa β-zink silikat pada suhu 700 °C dan rawatan haba pada suhu 750 °C dan 800 °C, α-zink silikat terhasil. Penghabluran meningkat dengan suhu rawatan haba. Analisis FESEM menunjukkan suhu rawatan haba bertambah, fasa kaca bertambah baik. Rawatan haba pada suhu 700 °C menunjukkan persambungan antara zarah-zarah terhasil dan pada suhu 750 dan 800 °C ketumpatan bertambah dan permukaan menjadi licin. Spektra FTIR menunjukkan kehadiran ZnO_4, SiO_4 dan Zn_2SiO_4 membuktikan pembentukan zink silika dan keamatan spektra FTIR meningkat dengan suhu. Tambahan pula, analisis UV-Vis untuk mengkaji kaca seramik zink silika mendedahkan sela jalur optik sampel. Kelebihan penyerapan beralih daripada panjang gelombang pendek ke panjang gelombang lebih besar dengan pertambahan suhu. Proses peralihan tersebut adalah disebabkan oleh pembentukan kristal zink silikat di dalam kaca. Manakala, sela jalur optik menunjukkan penurunan dengan suhu rawatan haba yang bertambah. Kristal zink silikat yang wujud di dalam sampel menyebabkan berlakunya penyerakan pada cahaya gelombang rendah. Peralihan yang diperoleh daripada sela jalur optik adalah $n = 3/2$. Maka dengan itu, sistem kaca ini boleh menjadi bahan fosfor yang berpotensi untuk peranti elektronik.

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TABLE OF CONTENTS

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LIST OF TABLES

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LIST OF FIGURES

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LIST OF ABBREVIATIONS

α	Alpha
β	Beta
B_2O_3	Boron oxide
DSC	Differential Scanning Calorimetry
E_{opt}	Optical band gap energy
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Reflection
PL	Photoluminescence
PVA	Polyvinyl alcohol
RE	Rare earth
RH	Rice husk
SiO_2	Silicon dioxide
SLS	Soda lime silica
T_g	Glass transition temperature
TM	Transition metals
UV-Vis	Ultraviolet-Visible
WRHA	White rice husk ashes
XRD	X-Ray Diffraction
ZnO	Zinc oxide
Zn_2SiO_4	Willemite

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CHAPTER 1

INTRODUCTION

1.1 Research background

Industry has been playing a big role in improving the technology used to meet the high demand by consumer. Agriculture and crop industry serve as main production industry to the consumer. Due to high demand of product by the consumer, industry take lead to improve the technology in order to obtain huge product within short time. The high demand is because of the increase population on the earth. However, this lead to high waste production without the proper waste management.

In Asian country especially Malaysia, rice is a staple food. Annually, the production of rice is more than 400,000 tons (Lee et al., 2013). Due to the enormous amount of production, the waste rice husk from the crop was extremely huge. However, most of the waste been discarded to the river or burnt in the paddy field by farmer (Al-Nidawi et al., 2017). Throwing away rice husk waste into the river cause the water pollution and can lead to flooding when heavy rain come.

Besides that, by burning the waste rice husk in an open burning at the paddy field lead to air pollution (Bakar et al., 2016). This is because, when being burnt the waste rice husk produced silica which is dangerous for health when being inhale. The burnt waste rice husk normally been use to fertilize the soil. However, it leads to dangerous health effect such as coughing, sore throat and even worse lung diseases (Lee et al., 2013). Therefore, researchers trying to find a way to overcome this problem. Research conducted try to utilize waste in glass making process because of the limited natural resources. Glass is an interesting material due to its useful as various applications such as solid state lasers and phosphor material.

Zinc silicate (Zn_2SiO_4) glass-ceramic also known as willemite are widely used as phosphor material in opto-electronic industry (Azman et al., 2018). Willemite has phenakite structure with rigid lattice that will enhance the optical properties (Sarrigani et al., 2015). Previously, willemite is found naturally at 1812 where the willemite doped with Mn. However, in current situation the naturally found willemite has been decreased therefore researchers trying to fabricate willemite using pure materials and produce it with glass-ceramic technique.

Willemite is famous as suitable host matrix for various rare-earth and transition metals. When being doped with rare earth ions and transition metals, the luminescence performance of the willemite improved (Tarafder et al., 2013). According to Takesue et al. (2009), previous Mn-doped willemite found exhibit green luminescence and widely

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used as phosphor in oscilloscope, colour television, fluorescent lamps and many more optic devices.
However, production of willemite at lower temperature are being crucial purpose for the researchers. Previous research stated that willemite has very high melting point approximately 1500 °C which is causing the production to consume very high energy (Omar et al., 2016b). Therefore, waste utilization in production of willemite help to reduce the energy consume. However, the researchers still trying to find a method that can be used to reduce more energy consume in fabrication of willemite.

In the current study, ternary glass system $ZnO–B_2O_3–SiO_2$ from waste rice husk are prepared by conventional melt and quenching method. The willemite produce by applying controlled heat treatment technique. The precursor glass and willemite glass-ceramic are investigated by its physical, structural and optical properties. The effect of ZnO/B_2O_3 ratio and ZnO/SiO_2 ratio on the properties of the glass and glass-ceramic are investigate. The physical properties are being studied by observing the density and linear shrinkage behavior. Meanwhile, the structural properties are investigate by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and fourier transform infrared reflection (FTIR) spectroscopy. On the other hand, optical properties are being study by UV-Visible (UV-Vis) and photoluminescence (PL) spectroscopy.

1.2 Problem statement

Production of willemite as phosphor material in previous research utilizing raw material of SiO_2. Commercialized SiO_2 has a very high purity which is 99.99% and that is costly for the research. Besides that, due to the fact of high purity of raw material the process of fabrication of willemite consume much more energy. In previous project, researchers required to fire the mixed well ZnO and SiO_2 at very high temperature because the melting point of raw materials are very high. Therefore, researchers try to find a way to solve this problem. In recent researches, researchers conduct fabrication of willemite utilizing waste material to replace raw SiO_2. Few suggestions of substituent for SiO_2 rise up such as soda lime silica (SLS) glass, rice husk (RH), coconut shell, palm oil and arica nut.

Waste RH has drawn a great attention because of its high purity of SiO_2 on the white rice husk ash (WRHA). WRHA can go up to 95 wt.% of SiO_2 according to previous research (Bakar et al., 2016; Lee et al., 2017; Al-Nidawi et al., 2017). WRHA has the closest value of purity to the commercialized SiO_2 presence. According to previous researches, the production of willemite from WRHA consume less energy. Takesue et al. (2009) reported that formation of willemite by using commercialized SiO_2 takes place at temperature 960 °C. Meanwhile, other researchers utilizing WRHA obtain willemite at 900 °C (Azman et al., 2018; Wahab et al., 2019; Khaidir et al., 2019). This prove that WRHA is the most prominent to be used as replace to commercialized SiO_2. Next, researcher widen the research for formation of willemite by adding B_2O_3 into the based glass.

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Kullberg et al. (2016) stated that B_2O_3 used to reduce the melting point of the glass. This is because B_2O_3 able to act as network former and able to reduce the melting point. Besides that, there are limited report on study of effect of B_2O_3 on the physical, structural and optical properties of ZnO-SiO_2 from WRHA glass system and willemite based glass-ceramic. Willemite is a promising phosphor in optoelectronic industry due to its large band gap, chemical stability, prominent host for dopant and wide range of UV-visible range (Zaid et al., 2016c). Willemite doped rare earth has been used as phosphor in oscilloscope, television, light emitting diode and various display and lighting devices.

Therefore, the aim of this project is to produce willemite at lower temperature. Thus, an investigation and study of the effect of B_2O_2 on the crystallization of willemite based glass-ceramic of ZnO–B_2O_3–SiO_2 ternary glass system derived from white rice husk ashes are carried out and the results of this research are expected to be used for future application as phosphor material.

1.3 Objectives

In this research, the purpose is to synthesis willemite from ZnO–B_2O_3–SiO_2 ternary glass system and utilizing SiO_2 source from waste material. This objective can be achieved by using various composition of the ternary glass system, melt and quenching method and heat treatment process.

This project was carried out by several objectives as follows:

1. To fabricate and synthesize of ZnO–B_2O_3–SiO_2 glass from waste rice husk.
2. To study the effect of ZnO/B_2O_3 and ZnO/SiO_2 ratio on physical, structural and optical properties of glass.
3. To investigate the effect of heat treatment temperature towards the structural and optical properties of willemite glass-ceramic.
4. To analyze the influence of B_2O_3 on the formation of willemite in the glass ceramic.

1.4 Scope of study

In this research, there is two series of glass being investigate. The scope of study are as follows:

1. ZnO–B_2O_3–SiO_2 ternary glass system was synthesized from waste rice husk, ZnO and B_2O_3 powders according to empirical formula of series 1 and series 2 by using conventional melt and quenching method. Empirical formula for series 1 is 55-x(ZnO)x(B_2O_3)45(WRHA) where x = 5, 10 and 15 wt.% meanwhile the empirical formula of series 2 is 85-y(ZnO)y(WRHA)15(B_2O_3) where y = 25, 30, 35 and 45 wt.%.
2. Zn_2SiO_4 glass-ceramic based ZnO-B_2O_3-SiO_2 for both series 1 and series 2 were heat treated at temperature 650 °C to 800 °C.

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3. The physical properties of Zn_2SiO_4 was investigate using electronic densimeter and vernier caliper to determine the density and the linear shrinkage of the samples respectively.
4. The structural properties of Zn_2SiO_4 was analyze using XRD, FTIR and FESEM to investigate the phase formation, chemical bonding presence and microstructure of the samples.
5. The optical properties of Zn_2SiO_4 was study using UV-Vis and PL to analyze the absorption, optical band gap and luminescence of the samples.

1.5 Thesis outline

This thesis consists of 5 chapters. Chapter 1 will be the introduction of general information about $ZnO–B_2O_3–SiO_2$ glass system and willemite glass-ceramic. Chapter 2 will discuss on the literature review on glass and glass-ceramic from previous and recent researches. Chapter 3 will explain in details about materials, apparatus method and characterization of $ZnO–B_2O_3–SiO_2$ ternary glass system and willemite glass-ceramic. Chapter 4 will discuss and analyze the results on investigation of effect of ZnO/B_2O_3 ratio and influence of heat treatment temperature on the structural and optical properties of $ZnO–B_2O_3–SiO_2$ glass and willemite glass-ceramic. Lastly, chapter 5 will present the conclusion of this research project and suggestions for further study.

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LIST OF PUBLICATIONS

Azman, A. Z. K., Matori, K. A., Ab Aziz, S. H., Zaid, M. H. M., Wahab, S. A. A., & Khaidir, R. E. M. (2018). Comprehensive study on structural and optical properties of Tm_2O_3 doped zinc silicate based glass–ceramics. *Journal of Materials Science: Materials in Electronics*, *29*(23), 19861-19866.

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Conferences

1. Participants at International Symposium of Applied Engineering and Science (SAES) Malaysia held from 14th November – 15th November 2017 at The TNCPI, Universiti Putra Malaysia, UPM Serdang, Selangor.

2. Poster presenter at International Fundamental Science Congress (i-FSC 2018), held from 23rd October – 24th October 2018 at RHR Hotel, Uniten, Kajang, Selangor.

3. Oral and poster presenter at Materials Technology Challenges 2019 (MTC 2019) on 27th March 2019 at Dewan Sri Harmoni, 5th College, UPM Serdang, Selangor.

Competitions

1. Gold Medal Award at Materials Technology Challenges 2019 (MTC 2019) on 27th March 2019 at Dewan Sri Harmoni, 5th College, UPM Serdang, Selangor.

2. Bronze Medal Award at Materials Technology Challenges 2019 (MTC 2019) on
27th March 2019 at Dewan Sri Harmoni, 5th College, UPM Serdang, Selangor.

3. Best Poster Award at Materials Technology Challenges 2019 (MTC 2019) on 27th March 2019 at Dewat Sri Harmoni, 5th College, UPM Serdang, Selangor.

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