Materials Research Express

PAPER

Optical studies of crystalline ZnO–SiO
2
devolved from pyrolysis of coconut husk

Muhammad Fahmi Anuar 1, Yap Wing Fen 1,2, Mohd Hafiz Mohd Zaid 1 and Nur Alia Sheh Omar 2

1 Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
2 Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
E-mail: yapwingfen@gmail.com

Keywords: optical, coconut husk ash, XRD, structural, zinc silicate

Abstract

In this paper, the ZnO–SiO
2
devolved from coconut husk ash by using conventional solid state method. The ZnO–SiO
2
crystal system was heat-treated. The presented results showed good properties of zinc silicate and it has a great potential as phosphors in optical application.

1. Introduction

Waste disposal is a complicated methodical process of removing nonessential materials including burial, burning, discharge and recycling. Waste materials were produced from various sources of operations such as factories, industries, mining operation, and agricultural sectors. These waste materials can be hazardous, toxic, corrosive and sometimes can be fatal to human. Thus, these obsolete items require appropriate waste management and disposal technique so that the problems can be contained since most countries have limited number of suitable disposal sites[ 1]. However, finding the best and innovative solution for effective management of waste require lots of time, energy and expense. Despite that, methods of recycling have been developed to minimize the harmful effects caused by landfill disposal and to convert the waste into variety of useful products.

Among the waste materials being recycled today, bio-waste is one of the most heavily studied because of its potential to be converted into raw materials. Bio-waste is defined as waste from living organisms, animals or plants. It is believed that major problems can arise if it is not disposed properly. Various researches have been conducted to ‘recycle’ bio-waste into materials that have potential to be used in certain applications. Among them were rice husk [2–6], rice straw [7–10], banana peel [11], corn cob [12, 13], palm waste [14, 15], sugarcane [16], turmeric [17], and coconut husk [18, 19]. Raw materials silica (SiO
2
) is one of the elements presents in most agricultural waste and commonly used in numerous researches for optical application especially in phosphors materials production. Therefore, production of phosphors materials from waste materials indeed solved the landfill problems at the same time provided a different route with less production cost.

One of the most promising candidates for phosphors materials is zinc silicate. Zinc silicate exhibits good luminescence properties and often used as a phosphors materials in numerous applications including fluorescent lamp, television, and displays materials or lighting appliances [20–22]. There are many advantages associated with the use of zinc silicates as optical host materials since they are able to acquire a wide range of multi-colors from luminescent activators [23]. Recent studies on zinc silicate showed that its absorbance and optical band gap value varied with the method of preparation. In addition, its optical properties can be altered by adjusting few parameters such as heat treatment, sintering temperature and dopant [2, 4, 24–26]. Commonly,
zinc silicate was synthesized using sol-gel method or solution precipitation method, which has the limitation due to the complicated process and higher cost of production. To overcome these issues, zinc silicate was synthesized by using solid-state reaction method, where waste coconut husk was used as the alternative silica source. In the nutshell, this research will greatly contribute the society by providing an alternative path of green synthesis method of producing zinc silicate phosphors from waste coconut husk. The optical properties of this novel ZnO–SiO2 product from the green synthesis will be explored.

2. Experimental procedure

2.1. Starting materials and synthesis

ZnO nanopowder (99.99%) (US Research Nanomaterials, Inc., United State of America) with range size of 10–30 nm and coconut husk ash (CHA) was used as the starting materials in this work. CHA was obtained from burned coconut husk at 700 °C for 2 h and after that undergone acid leaching process by sulphuric acid (H2SO4) to increase the silica composition to 91.76% [19]. ZnO and CHA were mixed together for 1 day using ball milling process to ensure the homogeneity of the mixed composition. After that, the mixture was pelleted and undergone heat treatment process at 1000 °C.

2.2. Characterization

X-ray diffraction analysis was carried out by using Phillips X’Pert High Pro PANanalytical Diffractometer (Malvern Panalytical, Almelo (Netherland) and Malvern (United Kingdom)) with set of data range from 2θ = 20° to 80°. Field emission scanning electron microscopy (FESEM) Nova NanoSEM 30 (FEI, Hillsboro, US) was used to study the morphological surface of the samples. The absorption spectra of the sample were determined by using UV-3600 Shimadzu (Shimadzu, Kyoto, Japan) in wavelength range from 220–800 nm. All measurements were carried out in room temperature.

3. Data analysis

FESEM analysis of the morphological structure of sample before and after heat treatment was performed with magnification level of 10 000 and 25 000. The micrograph in figure 1 clearly revealed that the surface morphology of the sample was not consistent and the shape of grains was irregular before applying the heat treatment. The sample size distribution was sporadic that probably due to the different size of starting materials used in the work. Contrary to sample before treatment, FESEM images of the samples after the heat treatment at 1000 °C (figure 2) have well-distinct boundaries. Undoubtedly, the heat treatment caused the sample to increase in size and produced larger crystal. The increased in grain size following the heat treatment was according to kinetic grain growth phenomenon [27]. With the increased in sintering temperature at constant holding time, the migration of crystal boundaries became more rapid thus increased the average grain size [28]. The sample was also no longer in irregular shape with no porosity observed in the figure due to the increase in the grain growth. This caused the particles to form neck with each other and agglomerated into bigger particles [24, 29]. Based on figures 1 and 2, the grain size was measured, where the average grain size for ZnO–SiO2 was 198 nm for sample before heat treatment, and it increased to 460 nm after heat treatment at 1000 °C.
The XRD pattern of ZnO–SiO₂ samples is shown in figure 3. All the diffraction peaks were matched with the standard value from Joint Committee on Powder Diffractions Standards (JCPDS). Before heat treatment, ZnO (JCPDS 14-0653) and SiO₂ (JCPDS 82-0511) were identified by the diffraction peaks emerged on the spectrum. On the other hand, different peaks started to emerge after heat treatment that can be assigned to zinc silicate (Zn₂SiO₄) (JCPDS 37-1485). This result is in good agreement with previous reported studies [30, 31]. Also, the peaks with higher diffraction intensity that can be observed after heat treatment depicted as high crystallinity of the zinc silicate. This is due to the high heat treatment temperature increased the atomic mobility that cause the grain growth and thus results in better crystallinity [32, 33].

The optical characterization was conducted to investigate the performance of ZnO–SiO₂ as potential phosphors materials. The optical properties of a metal nanostructures are determined by the collective oscillation of free electrons within the metal nanostructures, or known as plasmon. Its corresponding phenomenon is called surface plasmon resonance (SPR) [34]. The absorbance spectra of ZnO–SiO₂ before and after heat treatment are shown in figure 4. From the spectra, it can be seen that ZnO–SiO₂ showed the characteristic of SPR peak at around 364 nm and also a broad band at wavelength around 550–600 nm [35, 36]. This result is in good agreement with thus obtained by Bajpai et al [34] who found that ZnO nanoparticles exhibit a SPR peak around 364 nm. Apart from this, the absorption edge observed at wavelength 400 nm suggested that the absorption properties of the sample occurred in the UV region. It can also be observed that the absorbance intensity decreased and the absorbance edge was blue-shifted after the heat treatment at 1000 °C. The decrease in absorbance intensity at high temperature 1000 °C was due to the deformation of ZnO that leads to the formation of zinc silicate or ratio of crystallized/disordered ZnO [37]. It is known that the intensity of

**Figure 2.** FESEM images of crystalline ZnO–SiO₂ after heat treatment under magnification level of (a) 10,000 (b) 25,000.

**Figure 3.** XRD spectra of ZnO–SiO₂: (a) untreated (b) heat treated.
The absorbance band was highly dependent on ZnO content \cite{38}. The blue-shifted on the spectrum occurred due to high crystallinity of the zinc silicate sample when at high temperature of 1000 °C.

Based on the absorbance spectrum, the relation between the absorption coefficient, $\alpha$ and photon energy, $h\nu$ can be obtained by using the equation \cite{39, 40}:

$$\alpha(\nu) = \frac{(h\nu - E_g)^2}{h\nu}$$  \hspace{1cm} (1)

The equation (1) were rearranged into (2)

$$(\alpha h\nu)^{1/n} = h\nu - E_g$$  \hspace{1cm} (2)

$$(\alpha h\nu)^2 = h\nu - E_g$$  \hspace{1cm} (3)

Where $n$, is the type of transition, $h$ is the Planck’s constant, $\nu$ is the frequency and $E_g$ is the optical band gap. Different studies used different value of $n$, e.g. $n = 2$ used for amorphous semiconductor and for $n = 1/2$ was used in most crystalline semiconductor \cite{41}. In this work, $n = 1/2$ was used in equations (2) and (3) to determine the optical band gap of the sample based on the direct allowed transition. The band gap can be found by extrapolating the linear portion of the absorption curve until the x-intercept as shown in figure 5. From the
figure, the optical band gap of untreated sample was found to be 3.22 eV. However, the band gap value of heat-treated sample at 1000 °C were calculated at 4.05 eV. The improvement of the sample crystallinity as proven in the XRD analysis caused the reduction of delocalized states and thus making the sample with less defects resulting in increase of the optical band gap value [42].

4. Conclusion

In this work, ZnO–SiO2 crystal system was synthesized and investigated. Effect on heat treatment on the sample was discussed. The particle size of the sample measured from the FESEM analysis was 198 nm but increased to 460 nm after the heat treatment. In addition, the grains boundaries become more distinct after being sintered at 1000°C. Formation of zinc silicate crystalline system was determined by the diffraction peaks found on XRD spectrum after the sample was heat-treated. Lastly, the absorbance intensity of the sample decreased after the heat treatment. The optical band gap of untreated sample was 3.22 eV but increased significantly to 4.05 eV after the heat treatment.

Acknowledgments

The authors gratefully acknowledge the financial support for this study from the Malaysian Ministry of Education (MOE) and the Universiti Putra Malaysia (UPM) through the Putra Grant. The laboratory facilities provided by the Institute of Advanced Technology and Faculty of Science, Universiti Putra Malaysia, are also acknowledged.

Funding

The work was funded by Malaysian Ministry of Education (MOE) and the Universiti Putra Malaysia (UPM) through the Putra Grant 9642800. The fund was used for purchasing materials, apparatus and the characterization process fee.

Conflicts of interest

The authors declare no conflict of interest.

ORCID iDs

Yap Wing Fen @ https://orcid.org/0000-0003-3475-7469

References

[1] Zaid M H M, Matori K A, Wah I C, Sidek H A A, Halimah M K, Wahab Z A and Azmi B Z 2011 Elastic moduli prediction and correlation in soda lime silicate glasses containing ZnO Int. J. Phys. Sci. 6 1404–10
[2] Aisyah S et al 2019 Synthesis of cobalt oxide Co3O4 doped zinc silicate based glass- ceramic derived for LED applications Optik (Stuttg). 179 919–26
[3] Khaidir R E M, Fen Y W, Zaid M H M, Matori K A, Omar N A S, Anuar M F, Wahab S A A and Azman A Z K 2019 Exploring Eu3+-doped ZnO–SiO2 glass derived by recycling renewable source of waste rice husk for white-LEDs application Results Phys. 15 102596
[4] Lee C S, Matori K A, Ab Aziz S H, Kamari H M, Ismail I and Zaid M H M 2017 Fabrication and characterization of glass and glass-ceramic from rice husk ash as a potent material for opto-electronic applications J. Mater. Sci., Mater. Electron. 28 17611–21
[5] Kalapathy U, Proctor A and Shultz J 2001 A simple method for production of pure silica from rice hull ash Fuel Energy Abstr. 42 45
[6] Yuvakkumar R, Elango V, Rajendran V and Kannan N 2014 High-purity nano silica powder from rice husk using a simple chemical method J. Exp. Nanosci. 9 272–81
[7] Zaky R R, Hessien M M, El-Midany A A, Khedr M H, Abdel-Aal E A and El-Barawy K A 2008 Preparation of silica nanoparticles from semi-burned rice straw ash Powder Technol. 185 31–5
[8] Hessien M M, Rashad M M, Zaky R R, Abdel-aal E A and El-barawy K A 2009 Controlling the synthesis conditions for silica nanosphere from semi-burned rice straw Mater. Sci. Eng. B 162 14–21
[9] Khorsand H, Kiayee N and Masoomparast A H 2013 Optimization of amorphous silica nanoparticles synthesis from rice straw ash using design of experiments technique Part. Sci. Technol. 31 366–71
[10] Lu P and Hsieh Y L 2012 Highly pure amorphous silica nano-disks from rice straw Powder Technol. 225 149–55
[11] Ibrahim H M M 2015 Green synthesis and characterization of silver nanoparticles using banana peel extract and their antimicrobial activity against representative microorganisms J. Radiat. Res. Appl. Sci. 8 265–75
[12] Ọkoronkwọ E A, Imoziezi P E, Olubayode S A and Oluwatide S O 2016 Development of silica nanoparticle from corn cob ash Adv. Nanoparticles 05 135–9
Mater. Res. Express 7 (2020) 055901

[13] Adesanya D A and Raheem A A 2009 Development of corn cob ash blended cement Constr. Build. Mater. 23 347–52
[14] Faizal C P, Abdullah C and Fazilul B 2012 Review of extraction of silica from agricultural wastes using acid leaching treatment Adv. Mater. Res. 626 997–1000
[15] Faizal C P, Chik A and Bari M F 2016 Palm Ash as an alternative source for silica production MATEC Web Conf. 78 01062
[16] Norsuraya S, Fazlana H and Norhasyimy R 2016 Sugarcane bagasse as a renewable source of silica to synthesize Santa Barbara Amorphous–15 (SBA–15) Procedia Eng. 148 839–46
[17] Abdul Jalil R D, Nuaman R S, Abd A N, Abdul J, Nuaman R S and Aham A 2016 Biological synthesis of Titanium Dioxide nanoparticles by Curcuma longa plant extract and study its biological properties World Scientific 49 204–22
[18] Anuar M F, Fen Y W, Zaid M H M, Matori K A and Khadir R E M 2018 Synthesis and structural properties of coconut husk as potential silica source Results Phys. 11 1–4
[19] Anuar M F, Fen Y W, Matori K A and Mohd M H 2020 The physical and optical studies of crystalline silica derived from green synthesis of coconut husk ash Appl. Sci. 10 1–11
[20] Sarrigiani G V, Matori K A, Lim W F, Khazrmazi A, Quah H J, Bahari H R and Hashim M 2015 Structural and optical properties of erbium–doped willemite-based glass–ceramics Appl. Opt. 54 9925
[21] Takesue M, Hayashi S and Smith R L 2009 Thermal and chemical methods for producing zinc silicate (willemite): a review Prog. Cryst. Growth Charact. Mater. 55 98–124
[22] Ahmed T S, Haase M and Weller H 2000 Low-temperature synthesis of pure and Mn–doped willemite phosphor (Zn6SiO4: Mn) in aqueous medium Mater. Res. Bull. 35 1869–79
[23] Zhang Q Y, Pita K and Kam C H 2003 Sol-gel derived zinc silicate phosphor films for full-color display applications J. Phys. Chem. Solids 64 333–8
[24] Omar N A S, Fen Y W, Matori K A, Zaid M H M, Norhaizah M R, Nurzillah M and Zamratul M I M 2016 Synthesis and optical properties of europium doped zinc silicate prepared using low cost solid state reaction method J. Mater. Sci., Mater. Electron. 27 1092–9
[25] Azman A Z K, Matori K A, Aziz S H A, Wahab S A A and Khadir R E M 2018 Comprehensive study on structural and optical properties of Tm2O3 doped zinc silicate based glass–ceramics J. Mater. Sci., Mater. Electron. 29 19861–6
[26] Chakrabarti S, Ganguli D and Chaudhuri S 2004 Excitonic and defect related transitions in Zn2SiO4:Fe nanophosphors Optik (Stuttg.) 127 3727–9
[27] Radl N M, Fen Y W, Aziz S H A and Omar N A S 2017 Photoluminescence studies of cobalt (II) doped zinc silicate nanophosphors prepared via sol-gel method Optik (Stuttg.) 149 609–15
[28] Rashid S S A, Aziz S H A, Matori K A, Zaid M H M and Mohamed N 2017 Comprehensive study on sintering temperature on the physical, structural and optical properties of Er3+–doped ZnO–GSLS glasses Results Phys. 7 2224–51
[29] Syammini N F, Matori K A, Lim W F, Aziz S A, Hafiz M and Zaid M 2014 Effect of sintering temperature on structural and morphological properties of europium (III oxide doped willemite J. Spectrosc. 2014 1–9
[30] Saijip S K, Jadaun M and Tiwari S 2016 Synthesis, characterization and antimicrobial applications of zinc oxide nanoparticles loaded gum acacia/poly(SA) hydrogels Carbohydr. Polym. 153 60–5
[31] Olteanu N L, Rogozea E A, Popescu S A, Petcu A R, Lazhi M R, Mora M and Zamratul M I M 2016 Synthesis and optical properties of Zn2SiO4:Mn3+ erbium-doped willemite-based glass-ceramics J. Mater. Sci., Mater. Electron. 19 201
[32] Takesue M, Hayashi S and Smith R L 2009 Thermal and chemical methods for producing zinc silicate (willemite): a review Prog. Cryst. Growth Charact. Mater. 55 98–124
[33] Cortes J and Valencia E 1995 Phenomenological equations of the kinetics of heterogeneous adsorption with interaction between adsorbed molecules Phys. Rev. B—Condens. Matter Mater. Phys. 51 2621–3
[34] Naceur H, Megriche A and El Maaoui M 2014 Effect of sintering temperature on microstructure and electrical properties of SiO2 core–poly(SA) hydrogels Carbohydr. Polym. 153 60–5
[35] Olteanu N L, Rogozea E A, Popescu S A, Petcu A R, Lazhi M R, Mora M and Zamratul M I M 2016 Synthesis and optical properties of Zn2SiO4:Mn3+ erbium-doped willemite-based glass-ceramics J. Mater. Sci., Mater. Electron. 19 201
[36] Raevskaya A E et al 2014 Spectral and luminescent properties of ZnO–SiO2 core–shell nanoparticles with size-selected ZnO cores RSC Adv. 4 63593–401
[37] Xu L, Zheng G, Miao J, Su J, Zhang C, Shen H and Zhao L 2013 Regulating effect of SiO2 interlayer on optical properties of ZnO thin films J. Lumin. 136 307–12
[38] Engku Ali E G, Matori K A, Saion E, Aziz S H A, Zaid M H M and Albie I M 2018 Structural and optical properties of heat treated Zn2SiO4 composite prepared by impregnation of ZnO on SiO2 amorphous nanoparticles J. Phys. Chem. Solids, 11 75–85
[39] Tauc J, Grigorovici R and Vancu A 1966 Optical properties and electronic structure of amorphous germanium Phys. Status Solidi 15 627–36
[40] Hassani A S and Akl A A 2016 Effect of Se addition on optical and electrical properties of chalcogenide CdS:Se thin films Superlattices Microstruct. 89 153–69
[41] Shaaban E R, Aflify N and El-Taher A 2009 Effect of film thickness on microstructure parameters and optical constants of CdTe thin films J. Alloys Compd. 482 400–4
[42] Nazrin S N, Hamim M K, Muhammad F D, Yip J S, Hasnimuliyati L, Fazmny M F, Hazlin M A and Zaitzila I 2018 The effect of erbium oxide in physical and structural properties of tellurite glass system J. Non. Cryst. Solids 490 35–43