

SYNTHESIS AND CHARACTERIZATION OF ZINC SILICATE PRODUCED BY WET CHEMICAL METHOD

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ABSTRACT

In this study, zinc silicate was prepared by encapsulated silica powder, prepared from sodium silicate, with zinc nitrate hexahydrate in water. The obtained silica powder with average particle size of about 212.247 nm was mixed with zinc nitrate and the mixture of dried powder was subject to heat treatment at 600°C and 800°C. At 800°C, the XRD results showed the formation of zinc silicate phase. It was driven from the large surface area of silica powder that provide metastable state at a temperature lower than conventional solid state process. Although the zinc silicate phase was formed for the mixed ratio of Zn:Si at 2:1, ZnO and SiO₂ phases was not fully transform to α -Zn₂SiO₄ at 800°C since ZnO phase still can be observed. The PL spectrum exhibited blue and broad green emission peak due to the forming of oxygen-related centre on nano-structured silica and existing of both zinc oxide and zinc silicate phases.

Keywords: Zinc silicate; Willemite; Photoluminescence;

INTRODUCTION

Zinc silicate (Zn₂SiO₄) is a natural material and is known by its mineral name, willemite. The used of the doped zinc silicate as a phosphor in lightings and displays such as flourescent and neon lamps, televisions, oscilloscope and many other applications indicates that it is one of the important industrial material [1,2]. It has a promising future in advanced materials as a highly versatile luminescent material due to the wide range of multi-colors that can be obtained from various guest ions. The continuous improvement is still needed to increase the material efficiency. Zinc silicate is produced through conventional solid state reaction at high temperature and long processing time. It involves crushing, grinding, ball milling and sintering of source

material at very high temperature [3]. There are also other methods introduced by researchers in order to reduce the energy consumption during materials production and increases the properties of materials. Apart from chemical composition and crystal structure, size and dimensionality are now regarded as particularly important factors influencing the material properties [4]. The new methods that have been proposed such as sol-gel method [5], hydrothermal method [6] and polymer precursor method [7]. However, these methods require special equipment and expensive precursors, especially silica (SiO_2) precursor. The formation of zinc silicate can also be produced by embedding zinc precursors to nano size powder or porous silicon [8] and commercial mesoporous SiO_2 [9] follow by annealing at a certain temperature.

In this study, SiO_2 nanoparticle that is produced from precipitation of sodium silicate as a cheap precursor, mixed together with zinc nitrate hexahydrate as zinc precursor. The effect of heat treatment temperature to the mixture of zinc precursor with SiO_2 nano particle was studied by X-ray diffractometry, Fourier-transform infra-red spectrometer, particle size analyzer and photoluminescence techniques.

EXPERIMENTAL

Materials and Methodology

The SiO_2 powders were synthesized by modification of the method by [10]. Silica particle was obtained from a simple precipitation process with the reaction between ethanol (95%) and diluted sodium silicate solution ($\geq 10\%$ NaOH basis, $\geq 27\%$ SiO_2 basis from Sigma-Aldrich) in de-ionized water. The milky solution from the reaction was washed with de-ionized water a few times, vacuum filtered and dried in oven at 90°C for 24 hours. Zinc nitrate hexahydrate from Sigma-Aldrich was diluted in de-ionized water and dried silica powders was mixed at 2:1 ratio. The mixed solution was magnetically stirred for 2 hours and dried in oven. Then the dried powder was annealed at 600° and 800°C for 3 hours.

The prepared sample was analyzed by X-ray diffraction (XRD) with PANalytical X'pert Pro PW3050/60 diffractometer for phase identification, particle size was determined by Malvern Zetasizer Nano Series, Fourier Transform Infrared Spectroscopy (FT-IR) measurement was done with Perkin Elmer Spectrum 100 to identify functional group and bonding in powders and photoluminescence spectra were recorded with Perkin Elmer LS55.

RESULTS AND DISCUSSION

The preparation of silica powders for the precursors was based on the [10] method with a modification in order to get the fine distribution of nanopowder. The size of SiO_2 powder was measured with particle size analysis with the average particle size was about 212.247 nm as in Figure 1. The SiO_2 particle size obtained from measurement nearly two times of the previous method. The different in addition rate of the reaction mixture and stirring time, probably affected the nucleation and precipitation of the

particles. It was also reported by [10] that the particle was a hollow particle resulted from the washing with water instead of alcohol, although this feature is not reported in this study.

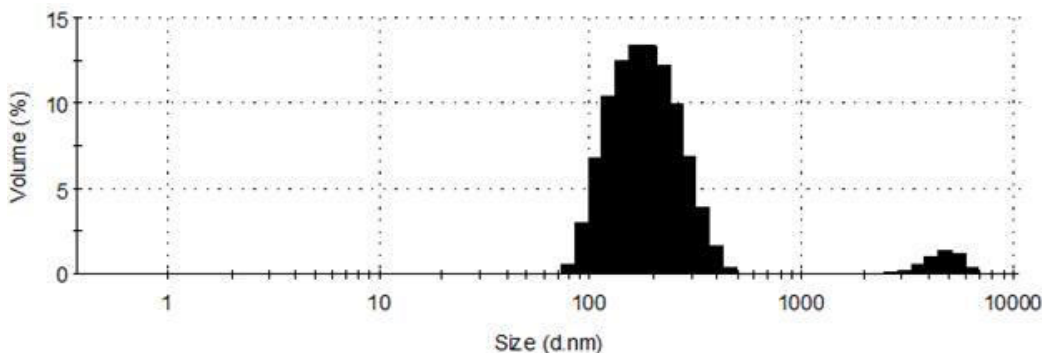


Figure 1: Particle size distribution of SiO₂ powder

The SiO₂ powder was mixed with zinc nitrate diluted in de-ionized water in order to incorporate zinc ions with SiO₂. After drying the solution mixture, the powder obtained was annealed at 600°C and 800°C for 3 hours. Figure 2 shows the FT-IR spectra of the mixed powder and also after the annealing. The main peaks in the spectrum of the dried powder of mixed SiO₂ and zinc nitrate precursor fall in the frequency range of 3600 to 300 cm⁻¹. For non heat treated mixed powder, broad frequency band in the range of 3670 to 2600 cm⁻¹ consist of the combination absorption of C-H, N-H and O-H bond vibrations. The peak at 1638 cm⁻¹ was from COO⁻ asymmetric molecule which is originated from ethanol (C₂H₄OH) absorption group [11]. Asymmetric stretching of the nitrates band (N-O) can be seen at the absorption peak of 1329 cm⁻¹ and in a broad frequency band is due to the nitrate ions from zinc nitrate [12]. The absorption peak at 1055 cm⁻¹ appeared in dried powder and for heat treated samples. The frequency corresponds to the absorption of Si-O-Si asymmetric stretching vibration [13,14]. Heat treatment of the samples at 600°C and 800°C shows the complete disappearing of organic compound revealing the complete decomposition of organic compounds and the behaviour of the dried powder toward heat. The Si-O-Si peak intensity reduced with the increase of treatment temperature. At 800°C, new peak emerge at 894 cm⁻¹ and 574 cm⁻¹ (Figure 2(c)) which is corresponds to asymmetric stretching vibration of SiO₄ group and symmetric stretching vibrations of ZnO₄ group respectively. The Si-O-Si which is made up of a surface silanols group (≡Si-OH) from the dried powder. The increasing heat applied to the samples, reducing the peak and also shifted the peak from 1055 cm⁻¹ to 1068 cm⁻¹ at 600°C and 1088 cm⁻¹ at 800°C. During high temperature treatment, the adjacent Si-O units and Zn ions in the mixed powder tends to form the symmetric changes and also involving with ions within the surroundings as reported by [15]. The decomposition of silanols, hydroxyl and organic functional groups at high temperature provide the different configuration of ions that would granted the shift in frequencies due to the ions motion. The existent of SiO₄ and ZnO₄ tetrahedron vibration band

attributed to the formation of Si-O-Zn linked in the heat treated samples which referred to the Zn_2SiO_4 phase formation as reported by [16] and confirmed by XRD analysis.

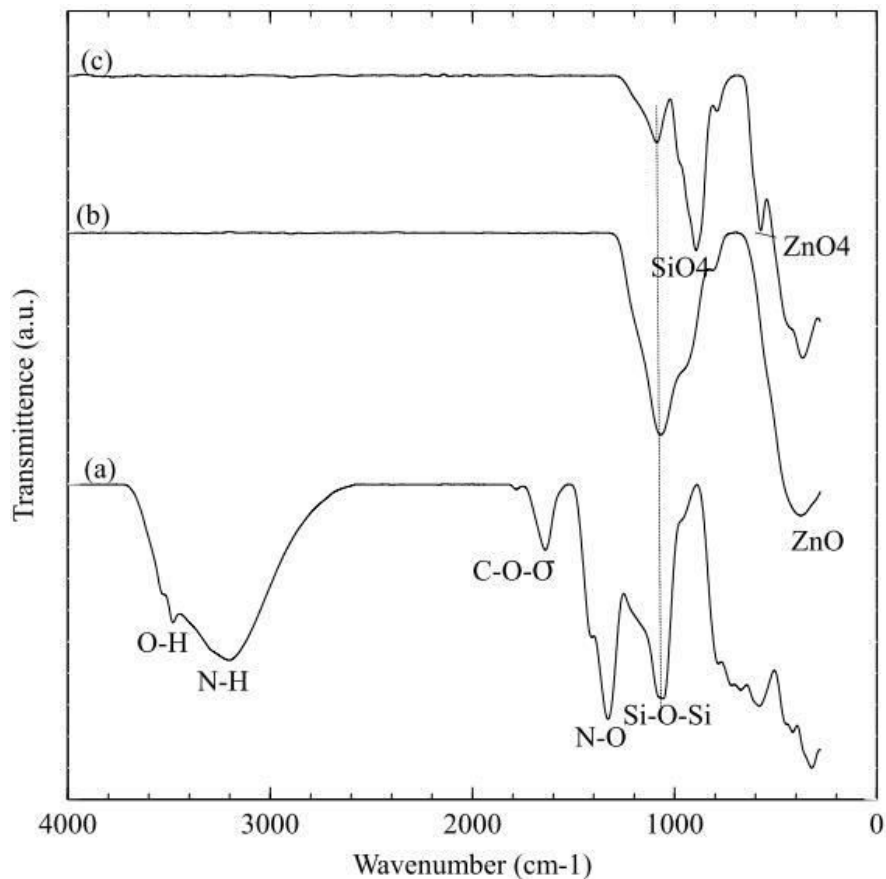


Figure 2: FT-IR spectra of (a) SiO_2 and zinc nitrate mixed powder, heat treated of mixed powder at (b) 600°C and (c) 800°C

The identification of phases was further strengthened by the XRD analysis as shown in Figure 3. The heat treatment of dried powder at 600°C indicates the crystalline ZnO reflection peak corresponding to the plane (100), (002), (011), (012), (110), (013), (020), (112) and (021), referred to the hexagonal wurtzite structure of ZnO (ICSD 98-001-1317). The SiO_2 phase cannot be detected by XRD since it was in the amorphous form. At 800°C heat treatment temperature, the formation of two crystalline phases was recognized as ZnO and $\alpha\text{-Zn}_2\text{SiO}_4$ (ICSD 98-000-5770). The increment of about 200°C of heat treatment temperature has induced the formation of $\alpha\text{-Zn}_2\text{SiO}_4$ phase. This observation is consistent with the FT-IR results that displayed the forming of Zn-O-Si band at the observed temperature [14]. The formation of $\alpha\text{-Zn}_2\text{SiO}_4$ phase at 800°C was highly depends on the time of treatment since [17] reported that only ZnO phase present at 15 minutes holding at that temperature and both phases emerge at 900°C .

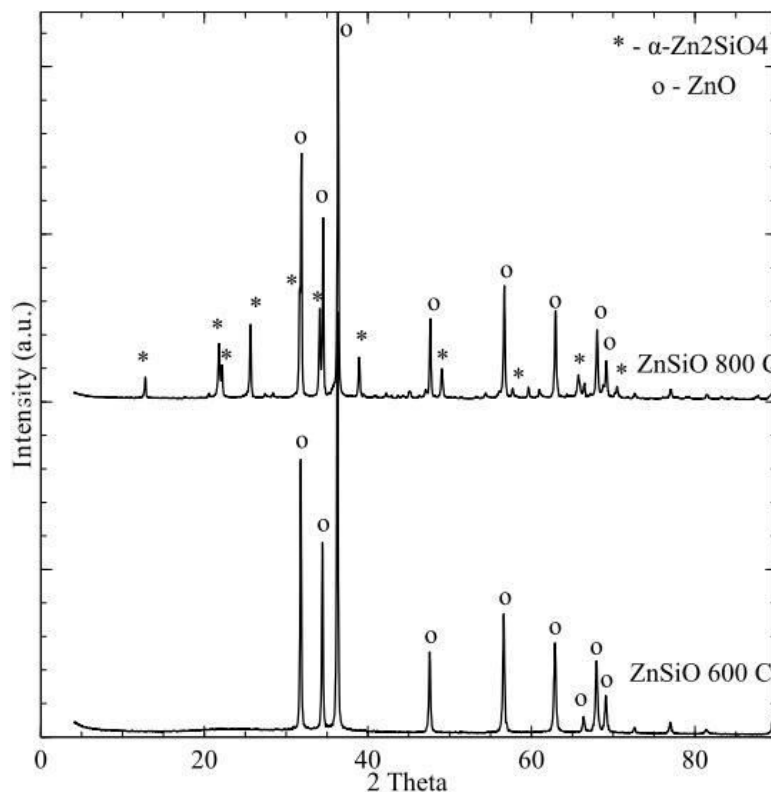


Figure 3 XRD diffractogram of heat treated samples at (a) 600°C and (b) 800°C

The used of organic based compound during the synthesis of dried powder of SiO₂ and mixed SiO₂ with zinc nitrate can lead to the transformation of structural defect evolution when heat treated. The optical properties of forming phases are prone to the formation of structural defect that causes by high temperature heat treatment. Figure 4 shows the photoluminescence spectra of heat treated samples at 600°C and 800°C for 3 hours. Both samples have the nearly same broad band emission peak at 422, 463, 482 and 530 nm wavelength. The 463 nm and 482 nm emission peak, which is in blue region emission was due to the forming of oxygen-related centres in nano-structured SiO₂ materials when exposed to high temperature heat treatment [18]. The emission peak within the violet spectrum range of 422 nm may be related to some intrinsic diamagnetic defect centre that comprises a simple oxygen vacancies and two folded-coordinated silicon [19]. The emission at 530 nm has a broad peak that was attributed to Zn₂SiO₄ and is consistent with previous report at 532 nm [20] and at 525 nm [21]. The wide band peak probably a consequence of green emission peak of ZnO since both of Zn₂SiO₄ and ZnO could easily overlapped especially when both of the phases exist together in this study as same as work done by [21].

By comparing to the conventional solid state reaction for the formation of Zn₂SiO₄, lower reaction temperature and time can be achieved by using the nanosize and porous SiO₂ with organic zinc precursors. The fine size of nano SiO₂ combined with the porous

morphology has elevated the Gibb's free energy to the metastable state due to the vast surface area [22]. This will adequately reduce the reaction activation energy and ease the reaction between the SiO_2 and ZnO . The removal of organic functional group, dehydration and dehydroxylation by heat treatment can activate the surface of the nano size powder to rearrange the structure that can lead to phase changes as shown for 800°C heat treated sample. Although at that temperature the $\alpha\text{-Zn}_2\text{SiO}_4$ phase has formed, the ZnO was still a dominant phase as shown by XRD diffractogram. The ratio of $\text{ZnO}:\text{SiO}_2$ at 2:1 is one of the subjected to be optimized together with treatment temperature and treatment holding time in order to get fully willemite phase.

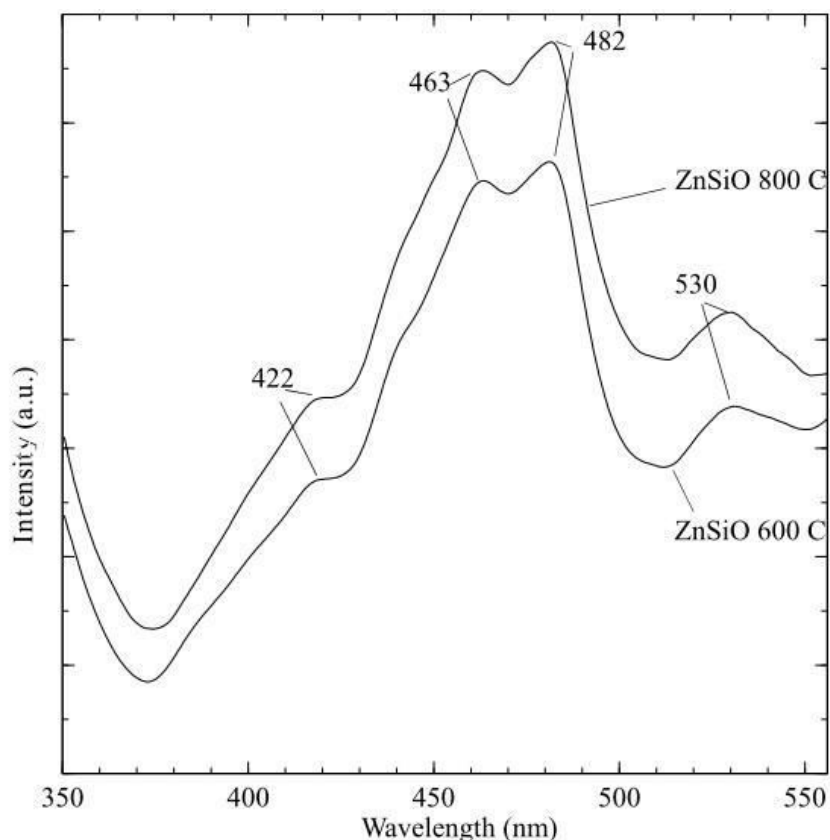


Figure 4: Photoluminescence spectra of heat treated samples at 600°C and 800°C measure at 320 nm excitation wavelength

CONCLUSION

In summary, the SiO_2 nano size particle made from sodium silicate was used as a source of SiO_2 with zinc nitrate hexahydrate to form zinc silicate. The heat treatment of dried precursor mixture with $\text{ZnO}:\text{SiO}_2$ ratio of 2:1 shows the crystalline ZnO phase at 600°C and emerging of $\alpha\text{-Zn}_2\text{SiO}_4$ phase together with ZnO phase at 800°C . The forming of $\alpha\text{-Zn}_2\text{SiO}_4$ at a lower temperature than conventional solid state method was due to the SiO_2 nano size particle that can drive phase change at much lower temperatures. The

ratio of ZnO:SiO₂, heating temperature and holding time can be optimized in order to obtain single Zn₂SiO₄ phase.

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