



NEAR INFRARED – EMITTING Zn_2SiO_4 POWDERS PRODUCED BY HIGH-ENERGY PLANETARY BALL MILLING TECHNIQUE

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ABSTRACT

The near infrared-emitting Zn_2SiO_4 powders were produced by high-energy planetary ball milling of ZnO and SiO_2 powders followed by annealing in air environment and at different temperatures. The surface morphology, crystal structure, chemical composition and optical properties of the obtained samples were investigated by means of field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), Raman spectroscopy and photoluminescence measurements (PL) at room temperature. The analysis indicates the formation of Zn_2SiO_4 phase with annealing temperature of 1250 °C. The size of Zn_2SiO_4 nanoparticles depends strongly on annealing temperature. Photoluminescence investigation reveals that the optimal annealing temperature for almost only near-infrared emission (~740 nm) is 1250 °C. The origin of this peak can be attributed to the energy transfer from non-bridging oxygen hole centers (NBOHs) to zinc interstitial (Zn_i) and oxygen vacancy (V_o) states in the Zn_2SiO_4 host lattice. These results demonstrate that we might be able to produce the Zn_2SiO_4 powders for applications in high CRI white light emitting diodes by a simple and low-cost method.

Keywords: Zn_2SiO_4 powders, photoluminescence of Zn_2SiO_4 , near infrared.

1. INTRODUCTION

Zinc silicate (Zn_2SiO_4) is a well known mineral that belongs to a large family of naturally occurring orthosilicates [1, 2]. The most thermodynamically stable one is α - Zn_2SiO_4 whose structure is made of $[SiO_4]^{4-}$ and $[ZnO_4]^{6-}$ tetrahedron. It has attracted much attention because of its unique luminescence properties, wide energy band gap (5.5 eV), excellent chemical stability, and highly saturated color [3, 4, 5]. α - Zn_2SiO_4 is one of the best candidates for numerous technological applications such as phosphor host, crystalline phase in glass ceramics, electrical

insulator, glazes, and pigments [3, 4, 5, 6, 7]. In addition, willemite (α - Zn_2SiO_4) is a promising host material for applications in the field of phosphors for light emitting devices.

With the development of materials technology, several physical and chemical synthesis techniques, such as: solid-state reaction, co-precipitation, sol-gel and combustion methods have been utilized to synthesize α - Zn_2SiO_4 [6, 8, 1]. Using sol-gel method, L. Shastri *et al.* have obtained ZnO – SiO₂ with the emission band at about 720 nm which could be assigned to the lattice disorder along the c-axis or transitions related to Zn_i [9]. By using sol-gel method combined with furnace firing, J. El Ghoul *et al.* have synthesized and studied luminescence of un-doped Zn_2SiO_4 [10]. The emission spectrum of Zn_2SiO_4 contains a strong and wide near infrared (NIR) emission band centered around 760 nm which can be connected with the formation of NBOHs excited at the spectral region $h\nu \geq 5.4$ (eV). Besides, in a study of the optical properties of ZnO nanostructures grown on SiO₂/Si substrate by thermal evaporation method, Tu Nguyen *et al.* have attributed the NIR emission around 730 nm to the energy transition from non-bridging oxygen hole centers of SiO₂ to Zn_i or V₀ states of Zn_2SiO_4 [10]. The origin of the NIR emission band have not been discussed throughly.

In this paper, we have synthesized willemite (α - Zn_2SiO_4) by high-energy planetary ball milling technique using ZnO and SiO₂ oxides as raw materials. The method is safe, instantaneous, low cost, and simple [11]. The properties of the samples were analyzed by XRD, SEM, Raman and PL measurements. The influence of synthesis conditions on the particle size and optical properties of willemite (α - Zn_2SiO_4) has also been studied. It is found that the obtained Zn_2SiO_4 powder emit strongly in the near infrared (740 nm). The origin of this near infrared emission band will be discussed in detail.

2. EXPERIMENTAL

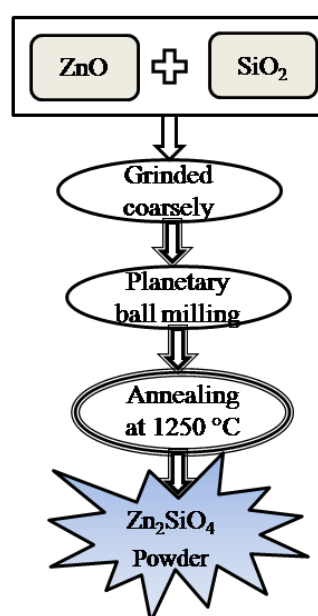


Figure 1. The process of producing Zn_2SiO_4 powder by high-energy planetary ball milling combined with annealing in air condition.

Commercial ZnO and SiO₂ powders (Merck) with purity of 99.0 % were used as starting materials. Firstly, mixture of ZnO and SiO₂ powder with weight ratio of 1:2 was grinded coarsely for 1 hour followed by high-energy planetary ball milling (Restch PM400) with the speed of 200 rpm for 40 hours and then annealed in air for 2 hours and at different temperatures from 900 °C to 1350 °C. The morphology was examined by ultra-high resolution scanning electron microscopy (Jeol JSM-7600F). The phase structure and crystallinity of samples were characterized by the X-ray diffraction (Bruker D8 Advance XRD). Chemical bonds were studied by using Raman measurements (Horiba Jobin-Yvon LabRAM HR Raman). Optical properties of all samples were investigated by a photoluminescence spectroscopy (Nanolog, Horiba Jobin Yvon, 450 W) at room temperature. The sample preparation process is shown in Figure 1.

3. RESULTS AND DISCUSSION

3.1. Material morphology

Figure 2 shows FESEM images of ZnO-SiO₂ powder with weight ratio of 1:2 after high-energy planetary ball milling for 40 hours (a) and after annealing at 1250 °C for 2 hours in air (b). From Fig. 2a, it can be seen that the initial ZnO-SiO₂ powder is broken down into pieces of a few tens of nanometers in size after ball-milling process. The particles size increases and reaches the average size of ~1 to 1.5 μm after annealing at 1250 °C for 2 hours in air environment (Fig. 2b).

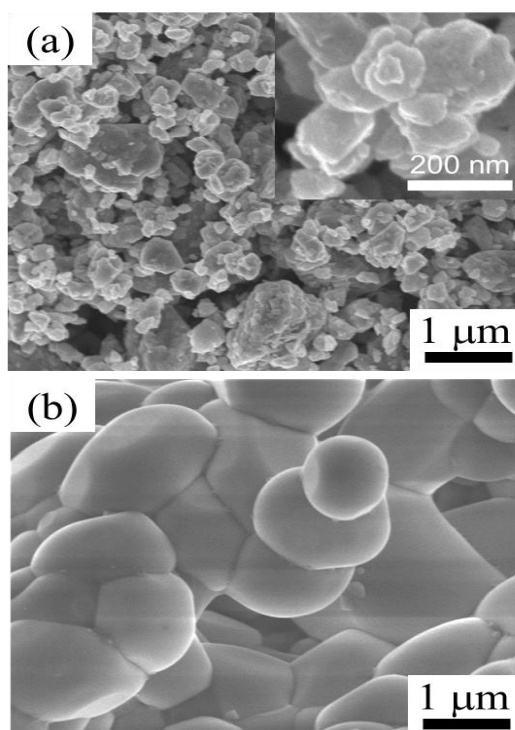


Figure 2. FESEM images of ZnO-SiO₂ powder with the weight ratio of 1:2 after high-energy planetary ball milling for 40 hours (a) and after milling and annealing at 1250 °C for 2 hours in air environment (b).

3.2. Material structure

Figure 3 displays X-ray diffraction (XRD) patterns of ZnO-SiO₂ powder after high-energy planetary ball milling for 40 hours and heat-treatment at different temperatures of 900 °C, 1250 °C, and 1350 °C for 2 hours in air environment. The XRD pattern of the non-heat treatment sample (see Fig. 3a) reveals two main sets of diffraction peaks which characterize ZnO and SiO₂ materials (JCPDF card No. 00-005-0664 and 00-027-0605, respectively). It means that ball-milling does not result in the formation of any new phase. When annealing sample at 900 °C, the characteristic peak of Zn₂SiO₄ phase has been observed, however, its intensity is still much smaller than one of silica and zinc oxide, as shown in Fig. 3b. From XRD patterns in Fig. 2(c,d), it can be seen that the Zn₂SiO₄ phase become dominant after annealing at 1250 °C and 1350 °C (JCPDF card 37-1485). This result indicates that the solid reaction between silica and zinc oxide has occurred during high temperature annealing process.

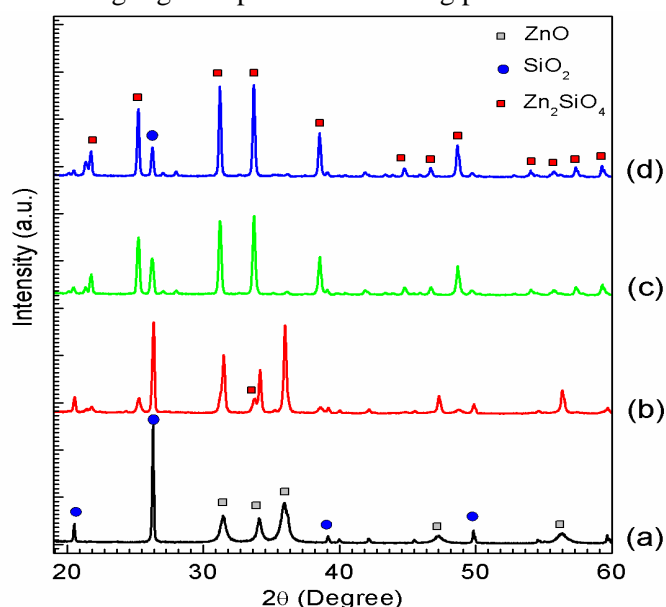


Figure 3. XRD patterns of ZnO-SiO₂ powders with weight ratio of 1:2 after high-energy planetary ball milling for 40 hours (a) and ZnO-SiO₂ sample after ball-milling and annealing at 900 °C (b), 1250 °C (c), and 1350 °C (d) for 2 hours in air environment.

3.3. Material vibrational spectra

Raman spectra of ZnO-SiO₂ powders after high-energy planetary ball milling for 40 hours and after annealing at 900 °C, 1250 °C, and 1350 °C for 2 hours in air are shown in Fig. 4. It can be seen that after ball-milling and heat-treatment at low temperature (900 °C), the spectrum shows vibrational modes at 433 cm⁻¹ and 460 cm⁻¹ which originate from Zn-O bond and siloxane link-age [12] of ZnO and SiO₂ materials, respectively. It is concluded that the willemite Zn₂SiO₄ has not been formed yet (see Fig. 4(a, b)). This is consistent with aforementioned XRD result. Fig. 4 (c, d) show Raman spectra of samples annealed at 1250 °C and 1350 °C, respectively. The Raman spectra contain vibrational modes at 348, 397, 868, 903 and 947 cm⁻¹ which correspond to the surface of siloxane group (the Si-O-Si linkage) and characteristics of Zn₂SiO₄ material [12]. This is also in good agreement with the XRD characterization result.

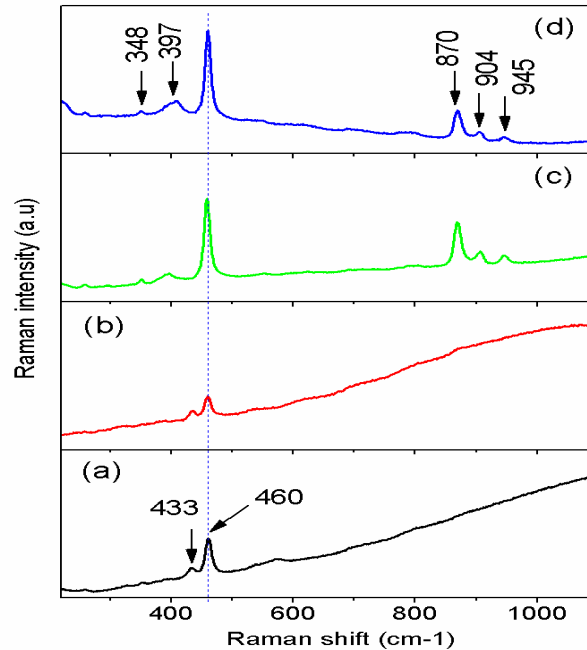


Figure 4. Raman spectra of ZnO-SiO₂ powder (with weight ratio of 1:2) after high-energy planetary ball milling for 40 hours (a) and ZnO-SiO₂ samples after milling and annealing at 900 °C (b), 1250 °C (c), and 1350 °C (d) for 2 hours in air environment.

3.4. Optical properties

Figure 5 shows PL spectra at room temperature of the ZnO-SiO₂ powder after high-energy planetary ball milling for 40 hours and after annealing at different temperatures for 2 hours in air environment. The PL spectrum of sample before heat treatment covers a broad wavelength range from 450 to 850 nm. The origin of this emission band can be attributed to defect-related emissions in ZnO or/and SiO₂ [13]. According to Lokesh Shastri *et al.* the broad green – red emission band found in the sample can be attributed either to oxygen interstitial defects or the transition from zinc interstitials (Zn_i) to oxygen interstitials (O_i) above the valence band [9]. For sample annealed at low temperature (900 °C), the weak emission peak appears around 540 nm can be attributed to defect-related emissions of ZnO and SiO₂ materials after ball-milling process, respectively (see inset in Fig. 5b). It means that under ball-milling and heat treatment conditions at 900 °C, the interaction between ZnO and SiO₂ has not been observed. This is in good agreement with the XRD and Raman results that we discussed above.

However, when the samples were annealed at higher temperatures (1150, 1250 and 1350 °C), their emission spectra show two broad bands centered at 525 nm and 740 nm. The former is attributed to ZnO or/and SiO₂ defects such as oxygen vacancy (V_o), zinc interstitials (Zn_i), oxygen interstitials (O_i) or/and other reasons [14, 15]. The latter has been reported and discussed in the previous studies [8, 16, 17]. For example, the NIR emission around 670-740 nm has been assigned to be related to V_o and Zn_i in some reports [16] while the origin of the peak at 760 nm is attributed to energy transfer from Zn₂SiO₄ particles to NBOHs interface defects in some others [4, 5, 7, 18]. Tu Nguyen *et al.* have explained the NIR emission at 730 nm as the result of the energy transition from NBOHs to Zn_i or V_o states in Zn₂SiO₄ particles [17]. This suggests that

the origin of NIR emission (around 740 nm) could be related to energy transfer from NBOHs interface defects to defect states in Zn_2SiO_4 particles. Besides, the annealing temperature of 1250 °C appears to be the optimal condition for the highest PL intensity of the NIR emission.

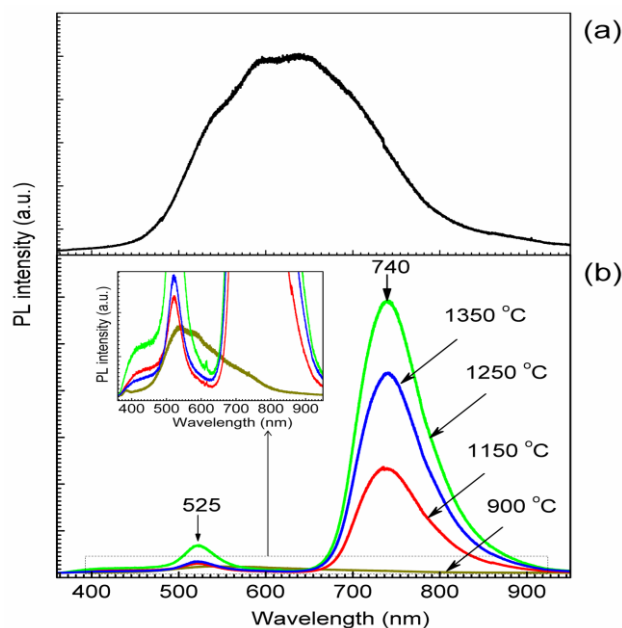


Figure 5. PL spectra of ZnO-SiO₂ powder with weight ratio of 1:2 after high-energy planetary ball milling for 40 hours (a) and after annealing at different temperatures for 2 hours in air environment.

4. CONCLUSION

Near infrared Zn_2SiO_4 phosphor has been produced successfully by high-energy ball milling technique followed by annealing in air. The XRD and Raman measurements reveal the formation of Zn_2SiO_4 phase with the annealing temperature of 1250 °C. This high-temperature annealing powder emits intensively in the near infrared peaking at 740 nm. The origin of this emission is has been interpreted as due to energy transfer from NBOHs interface defects to defect states in Zn_2SiO_4 crystalline powder. Being simple to produce and with strong NIR emission intensity, the Zn_2SiO_4 powder obtained in our experiment is a potential NIR component for high CRI white light emitting diode.

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