TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC QUY NHƠN

Vật liệu $Zn_2Sio_4:Mn^{2+}$ hấp thụ mạnh ánh sáng xanh chế tạo bằng phương pháp nghiền bi hành tinh năng lượng cao

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TÓM TẮT

Bài báo trình bày kết quả nghiên cứu tính chất quang phát quang và nhiệt phát quang của vật liệu Zn_2SnO_4 pha tạp ion Mn^{2+} chế tạo bằng phương pháp nghiền bi hành tinh năng lượng cao kết hợp ủ nhiệt tại 1250°C. Cấu trúc và tính chất của vật liệu được khảo sát bằng các phương pháp nhiễu xạ tia X bột (PXRD), ảnh hiển vi điện tử phát xạ trường (FESEM), phổ phát quang (PL) và phổ nhiệt phát quang (TL). Phổ phát quang của vật liệu chế tạo được cho phát xạ ánh sáng xanh với cực đại phát xạ tại 525 nm do chuyển dời điện tử $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ của ion Mn^{2+} trong mạng nền Zn_2SiO_4. Phổ kích thích phát quang cho hấp thụ mạnh tại các bước sóng 270 nm, 356 nm, 377 nm, 420 nm, 432 nm và 470 nm, trong đó vật liệu hấp thụ mạnh nhất ở bước sóng trong vùng ánh sáng xanh 420 nm. Vật liệu có khả năng ứng dụng trong chế tạo LED sử dụng chip LED xanh lục với cơ chế hấp thụ ánh sáng xanh lục sang ánh sáng xanh lá cây.

Từ khóa: *Vật liệu Zn_2SiO_4: Mn^{2+}, tính chất quang và nhiệt phát quang của vật liệu Zn_2SiO_4: Mn^{2+}, Zn_2SiO_4 pha tạp Mn^{2+}, vật liệu hấp thụ ánh sáng xanh da trời phát xạ xanh lá cây.*

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Strong blue absorption of Zn_2SiO_4:Mn^{2+} prepared by high-energy planetary ball milling technique

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ABSTRACT

The paper presents the results of the photoluminescence and thermoluminescence behaviour of Mn^{2+}-doped Zn_2SiO_4 powder synthesized by high - energy planetary ball milling technique followed by calcination in air at 1250 °C. The obtained phosphor was characterized using powder X-Ray diffraction (PXRD), field emission scanning electron microscopy (FESEM), photoluminescence (PL) and thermo- luminescence (TL) techniques. The PL spectrum illustrates the emission centered at 525 nm corresponds to the $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition of Mn^{2+} in the host Zn_2SiO_4 crystal. The photoluminescence excitation spectra present six excitation bands peaking at 270 nm, 356 nm, 377 nm, 420 nm, 432 nm and 470 nm, respectively, in which the strongest absorption belongs to 420 nm wave length showing potential application of the prepared phosphor in white-light-emitting diode as a blue-to-green color conversion phosphor.

Keywords: *Zn_2SiO_4: Mn^{2+} powders, PL and TL of Zn_2SiO_4: Mn^{2+}, green phosphor, Mn^{2+} doped Zn_2SiO_4, blue-to-green color conversion phosphor*.

1. INTRODUCTION

Zn_2SiO_4 a well known mineral of naturally occurring orthosilicates family has attracted much attention because of its unique luminescence properties, wide energy band gap (5,5 eV), excellent chemical stability, and highly saturated color.[1-5] It may exist in several crystaline forms such as α, β and other phases. In which, 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.[3-7]

Rare-earth ions are considered as excellent luminescence centers so most phosphors for LED application are mainly based on rare earth phosphors. Rare earth doped zinc silicates have been studied extensively as efficient luminescence materials.[8,9] However, because of its expensive price, it is necessary to find such cheaper alternative materials holding a comparable luminescent efficiency. Among them, transition metal ions are the best candidate. Specifically, Mn^{2+} ion is regarded as a luminescence center, giving green - emission for α- Zn_2SiO_4 phase[10, 11] or yellow - emission for β- Zn_2SiO_4 phase[12, 13]. It is well known that depending on the strength of surrounding crystal field of Mn^{2+}, Mn^{2+} doped Zn_2SiO_4 generates a green or yellow emission because of the d-d transition from the $^4T_1(^4G)$ excited-state to the $^6A_1(^6S)$ ground-state in the 3d outer-most

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orbital.[11, 14] Although many previous works studied on the photoluminescence properties of Mn^{2+} doped Zn_2SiO_4 for numerous application,[7,10,15, 16] there are a few reports which discussed on its thermoluminescence.[8, 17] Besides, many methods have been applied to produce Mn-doped α- Zn_2SiO_4 phosphor.[10,11,18,19] Every method has its own benefits. High–energy planetary ball milling process supplies a lot of advantages such as low-cost, stable and simple method.[20]

In this work, the green emitting Zn_2SiO_4:Mn^{2+} powders were prepared by high - energy planetary ball milling of ZnO, SiO_2 and MnO_2 materials followed by annealing at 1250 °C in air environment. The PL spectra and luminescence decay curve show strong green emission with long life time. The PLE spectra represent a strong blue absorption at 420 nm which gives a potential application in WLED using blue LED chip.

2. EXPERIMENTAL

Commercial ZnO, SiO_2 and MnO_2 powders with purity of 99.99%, 99% and 99%, respectively were used as the starting materials. They were introduced into a 500 ml bowl consisting of 30 hardened steel balls. Then, the mixture was grinded coarsely for 1 hour and further grounded by high-energy planetary ball milling (Restch PM400) with the speed of 200 rpm for 40 hours. The whole process is carried out in air atmosphere at room temperature. Finally, this mixture was calcined in air for 2h at 1250 ^{0}C to obtain the fine Zn_2SiO_4: Mn^{2+} powder. The morphology was examined by ultra-high resolution scanning electron microscopy (Jeol JSM-7600F), the phase structure and the crystallinity of samples were characterized by the X-ray diffraction (Bruker D8 Advance XRD). Optical properties of all samples were investigated by photoluminescence spectroscopy (Nanolog, Horiba Jobin Yvon, 450 W) at the room temperature. Thermally stimulated luminescence glow curves were recorded at room temperature by using TLD reader. The obtained phosphor under the TL examination is given by β-ray beam (Sr90) radiation.

3. RESULTS AND DISCUSSION

Figure 1 displays X-ray diffraction (XRD) pattern of Zn_2SiO_4 powder after high-energy planetary ball milling for 40 hours and anneal at 1250 ^{o}C for 2 hours in air environment. It can be seen that the sample exhibits main diffraction peaks corresponding to (110), (211), (300), (220), (131), (312), (410), (223), (502), (600), (520), (333), (125), (710) (006), (630) and (713) of willemite Zn_2SiO_4. This result is well matched with other reports.[1-5]

Ultra-high resolution scanning electron microscopy (SEM - Jeol JSM-7600F) is an equipment which applied to determine the morphology and size of the sample as shown in figure 2a. SEM micrograph shows a fine morphology with nearly spherical particles of about 1 μm in average size. In addition, the compositions of the powder are also measured using Energy dispersive X-ray spectroscopy (EDX) during the FESEM observation (see figure 2b). As can be seen from the figure 2b, coupled with such obvious Si, Zn and O signals, Mn^{2+} ion is clearly recorded in the prepared sample and the atom percentage shows a suitable formation of Zn_2SiO_4. On the basis of XRD and EDX results, we can conclude that the pure Zn_2SiO_4: Mn^{2+} powder has been prepared successfully by high-energy ball milling technique followed by calcination in air at 1250 °C in air environment.

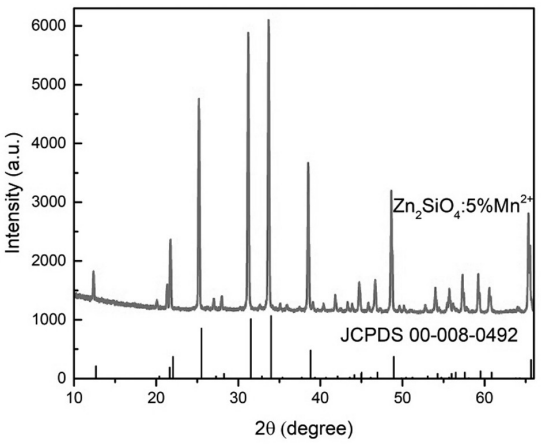

Figure 1. XRD pattern of Zn_2SiO_4:5%Mn^{2+} calcinated at 1250 °C

The excitation photoluminescence (PLE) spectra (figure 3a) and photoluminescence (figure 3b) of the Zn_2SiO_4:Mn^{2+} were recorded with the emission/excitation wavelength of 525/270 nm at room temperature by Nanolog - Horiba Jobin Yvon equipment. The excitaion spectrum (figure 3a) shows five strong absorption peaks at about 356 nm, 377 nm, 420 nm, 432 nm and 470 nm which assigned to the absorption peaks of the Mn^{2+} ion in the Zn_2SiO_4 lattice of $^6A_1(^6S) \rightarrow ^4E(^4D)$, $^6A_1(^6S) \rightarrow ^4T_2(^4D)$, $^6A_1(^6S) \rightarrow ^4E(^4G)$, $^6A_1(^6S) \rightarrow ^4T_2(^4G)$ and $^6A_1(^6S) \rightarrow ^4T_1(^4G)$, respectively[21, 22]. When using all these five excitation wavelengths as excited source, all five emission spectra (figure 5b) display green luminescence band centered at 525 nm which assigned to an electronic transition of $^4T_1(^4G) \rightarrow ^6A_1(^6S)$ of Mn^{2+} ions.[10,11] The highest PL intensity belongs to the 420 excitation wavelength attributed to $^4E(^4G) \rightarrow ^6A_1(^6S)$ which can apply for display application excited by blue LED.[3,11,18] Combined the PLE and X-ray diffraction results, we can confirm that Mn^{2+} ions have been substituted into the Zn^{2+} sites in the Zn_2SiO_4 host crystal which act as luminescence centers, giving green emission at 525 nm.

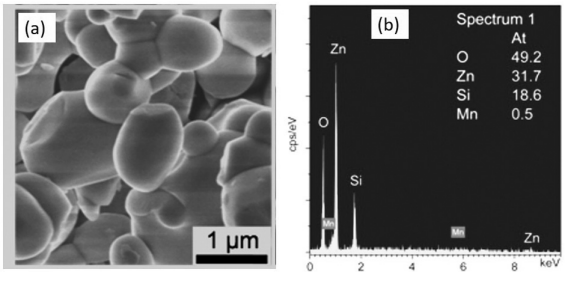

Figure 2. SEM image and EDS spectra of Zn_2SiO_4:Mn^{2+} calcinated at 1250 °C

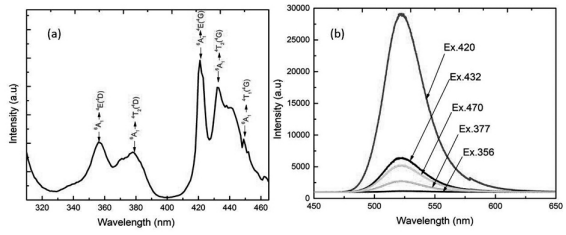

Figure 3. PLE (a) at the emission wavelength 525 nm and PL spectra (b) excited by various of excitation wavelength of Zn_2SiO_4: Mn^{2+} calcinated at 1250 °C

Thermoluminescence (TL) spectra of the prepared phosphor measured using β-ray beam (Sr90) source irradiation for 2, 5, 10, 15, 20 minutes and heating rate of 2 °C.s^{-1} are presented in figure 4. The TL intensity increases with increasing the X-ray exposure time. This is generally due to the competition between radiative and non-radiative centers, or between different kinds of trapping centers.[8] As TL theory[23, 24], the main basis in the thermoluminescence dosimetry (TLD) is that the TL output is directly proportional to the radiation dose received by the phosphor and hence provides the means of estimating the dose from unknown irradiations so the TL results of obtained sample show high potential application in TLD.

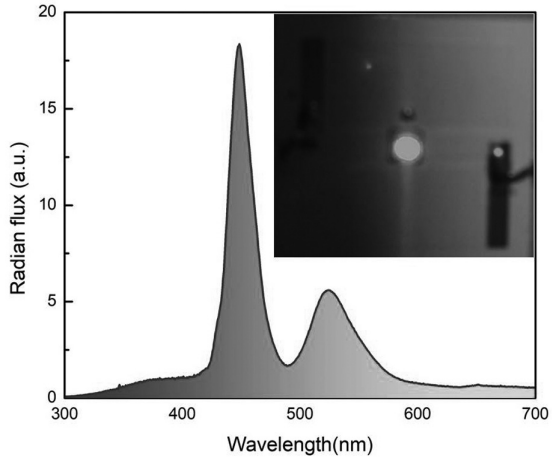

Figure 4. Photoluminescence spectra of Zn_2SiO_4: Mn^{2+} phosphor coated on 450 LED CHIP

It is well-known that LED is one of the most effective light and it is used widely today because of their physical, thermal and chemical stability.[24] As mentioned above, our investigation aims to produce a cheap phosphor excited by blue Chip employing a simple method. Accordingly, the Mn^{2+} doped Zn_2SiO_4 powder has been coated on LED chip 450 nm by i-DR S320A Desktop Dispensing system. The LEDs was supplied with a current of 0.1500A and a voltage of 3.029V during the process. Photoluminescence spectra and image of LED light are displayed in figure 5. This demonstrates that the pure green colour from obtained sample can be used for mixing with red phosphor on blue LED Chip to form WLED with high CRI.

4. CONCLUSION

Herein, the present research has studied the optical characteristics and thermoluminescence properties of Zn_2SiO_4:Mn^{2+} in detail. For photoluminescence, combined PLE, PL spectra, X-ray diffraction and EDS results demonstrate that Mn^{2+} ions are substituted into the Zn^{2+} sites in the Zn_2SiO_4 host crystal which act as luminescence centers, giving green emission at 525 nm. This photoluminescence enhancement under 420 nm enables application to WLED using blue LED Chip excitation.

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