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Controlled synthesis and relationship between luminescent properties and shape/crystal structure of Zn_2SiO_4:MN^{2+} phosphor

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Abstract

Mn-doped Zn_2SiO_4 phosphors with different morphology and crystal structure, which show different luminescence and photoluminescence intensity, were synthesized via a low-temperature hydrothermal route without further calcining treatment. As-synthesized zinc silicate nanostructures show green or yellow luminescence depending on their different crystal structure obtained under different preparation conditions. The yellow peak occurring at 575 nm comes from the β-phase zinc silicate, while the green peak centering at 525 nm results from the usual α-phase zinc silicate. From photoluminescence spectra, it is found that Zn_2SiO_4 nanorods have higher photoluminescence intensity than Zn_2SiO_4 nanoparticles. It can be ascribed to reduced surface-damaged region and high crystallinity of nanorods.

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Keywords: Fluorescence spectroscopy; Luminescence; Silicates; Crystal growth; Nanostructures

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1. Introduction

Recently, much research has been focused on the synthesis and characterization of one-dimensional (1D) nanomaterials [1–4]. Nanometer-sized inorganic 1D systems exhibit a wide range of optical and electrical properties [5]. Quantum confinement of electrons in 1D system provides a powerful tool for manipulating their optical, electrical, and thermoelectrical properties [6,7]. Most of these functions depend strongly on the chemical composition and crystal structure of materials. Novel properties would be obtained while the crystal structure of host materials was changed. However, size and dimensionality are

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now regarded as particularly important factors influencing the chemical and physical properties of the materials [8]. If materials were prepared in the form of a 1D nanostructure, they would be expected to be highly functionalized materials as a result of both shape-specific and quantum confinement effects, acting as electrically, magnetically, or optically functional host materials as well. However, the influences of crystal structure/shape on the luminescent properties are less reported.

Over the last decade, luminescent properties of inorganic phosphors have been extensively investigated to make flat panel displays more commercially available [9,10]. It is highly desirable to develop novel low-voltage phosphors with high efficiency and chemical stability under electron beam bombardment in a high-vacuum system for next generation field emission displays [11,12]. Mn-doped Zn_2SiO_4 is a well-known phosphor for its high luminescent efficiency and chemical stability, and has been used as a luminescent material for lamp and cathode ray tubes [13]. Many methods have been used to synthesize Mn-doped Zn_2SiO_4 phosphors [14–19]. But, few works reported the synthesis of 1D Mn-doped Zn_2SiO_4 and investigated the relationship between shape/crystal structure and photoluminescence properties.

Herein, we synthesized Mn-doped Zn_2SiO_4 phosphor with different shape/crystal structure via a low-temperature hydrothermal route without further calcining treatment. The effects of crystal structure or shape on the PL properties were also investigated. The as-synthesized Zn_2SiO_4:Mn^{2+} phosphors are green or yellow luminescence depending on the process conditions. This phenomenon comes of the different crystal structures of Zn_2SiO_4. The shape change of phosphors has a certain extent influence on their luminescent intensity.

2. Experimental section

All reagents were purchased from Shanghai Chemical Reagent Co. and used without further purification. In a typical procedure, 1 g sodium dodecyl sulfonate (SDS), 8 mmol $ZnCl_2$ and 0.24 mmol $MnCl_2 \cdot 4H_2O$ were dissolved in a mixture of 5 ml distilled water and 20 ml absolute ethanol in a beaker. Then the solution was dropped into 20 ml ethylenediamine under stirring in a Teflon liner of 60 ml capacity. After about 10 min, the aqueous solution of 4 mmol $Na_2SiO_3 \cdot 9H_2O$ dissolved in 5 ml distilled water was slowly added. The liner was sealed in a stainless-steel autoclave, first aged at 90 °C for 12 h, and then maintained at 220 °C for 6 days. After quenched with water to room temperature quickly, the resulting white solid products (sample c) were filtered off, washed with distilled water and absolute ethanol for several times, respectively, and finally dried in vacuum at 60 °C for 4 h. For comparison, one experiment (sample b) was carried out through a procedure which was similar to the above procedure except of the autoclave cooled to room temperature in air; another experiment (sample a) without SDS and air cooling to room temperature was processed under similar conditions.

The phase purity and phase structure of as-prepared samples were characterized by the X-ray powder diffraction (XRD) patterns, using a Philips X'pert X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The transmission electron microscopy (TEM) images and corresponding selected area electron diffraction (SAED) patterns were performed with a Hitachi H-800 transmission electron microscope using an accelerating voltage of 200 kV. Photoluminescence (PL) spectra were recorded on a Hitachi 850 fluorescence spectrometer with an Xe lamp at room temperature.

3. Results and discussion

Fig. 1 shows emission spectra for green and yellow luminescence at room temperature. The green luminescence is the conventional green of Zn_2SiO_4:Mn^{2+} phosphor, occurring at about 525 nm. The yellow luminescence main peak centers at 575 nm and there is still a weak peak at 525 nm (Fig. 1c). To compare the intensity of photoluminescence, it can be seen that the high PL

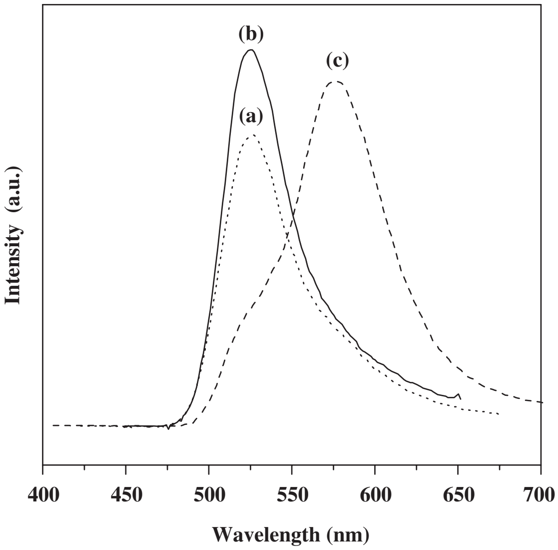

Fig. 1. Emission spectra of the Mn-doped Zn_2SiO_4 phosphors prepared in different conditions: (a) sample a—no SDS and cooled in air; (b) sample b—added SDS and cooled in air; (c) sample c—added SDS and quenched with water.

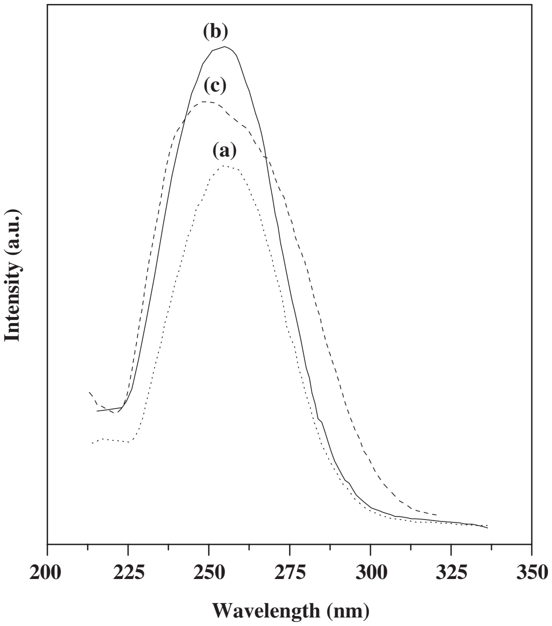

Fig. 2. Excitation spectra of the Mn-doped Zn_2SiO_4 phosphors prepared in different conditions: (a) sample a—no SDS and cooled in air; (b) sample b—added SDS and cooled in air; (c) sample c—added SDS and quenched with water.

intensity was obtained while surfactant SDS was added. The green and yellow photoluminescence come from the Mn impurities in the zinc silicate host material, and corresponding to the $^4T_1 \rightarrow {}^6A_1$ transition [20]. The luminescence of the Mn^{2+} ion is known to change depending on the host crystal field, covering a wide range from blue–green to red. Increasing the crystal field reduces the energy difference of the ground and first excited state, resulting in red-shift of the luminescence [21]. The appearance of yellow luminescence is basically an effect of the higher crystal field.

The excitation spectra for green and yellow luminescence at room temperature are provided in Fig. 2. From the excitation spectra, it can be seen that they are almost similar. There is an excitation band appearing at wavelengths shorter than 300 nm. This indicates that the luminescence for green and yellow emission results from a same source, i.e. Mn^{2+} ions. However, the peak maximum of excitation spectrum for yellow luminescence is blue shift compared to the green one. This implies that Mn^{2+} ions in yellow emitting sample feel a stronger crystal field, so higher energy is necessary to excite yellow emission. This result is in accordance with that of emission spectra. To compare the intensity of excitation spectra, it is found that there is an analogous intensity relation with that of emission spectra.

Fig. 3 shows the XRD patterns of the Mn-doped Zn_2SiO_4 phosphors synthesized at different conditions. Sample a (no SDS and cooled in air) and sample b (added SDS and cooled in air) can be indexed to a same phase. All the diffraction peaks of the as-synthesized samples can be indexed to a pure hexagonal structured Zn_2SiO_4 (α-phase) with cell constants of $a = 13.92$ Å, and $c = 9.34$ Å, which are in good agreement with the values in the literature (JCPDS card no. 37-1485, $a = 13.93$ Å, and $c = 9.31$ Å). No obvious impurity phase can be detected. Pattern c (added SDS and quenched with water) represents a totally different phase and has an approximate correspondence with the β-phase of Zn_2SiO_4 (JCPDS card no. 19-1479). Several weak peaks in pattern c can be

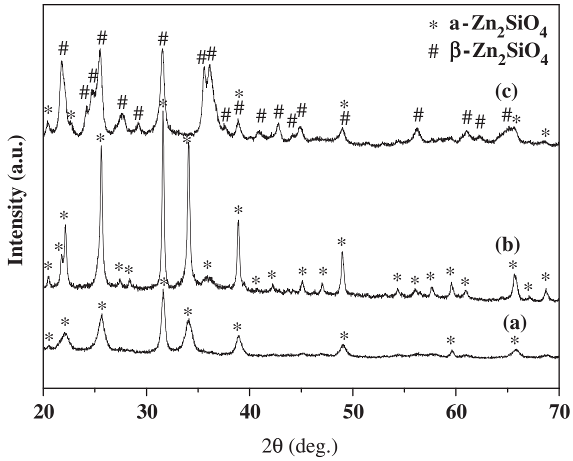

Fig. 3. XRD patterns for samples synthesized at different conditions: (a) sample a—no SDS and cooled in air; (b) sample b—added SDS and cooled in air; (c) sample c—added SDS and quenched with water.

index to α-phase of Zn_2SiO_4. β-Zn_2SiO_4 is a metastable phase, which occurs under certain processing conditions. For instance, melting and rapid cooling of near eutectic compositions of SiO_2 and ZnO results in the formation of β-phase [22]. At room temperature, β-Zn_2SiO_4 is quite stable, and only at high temperature does it transform to α-phase. In our procedure, water quenching is necessary to obtain β-Zn_2SiO_4. Because the cooling rate is still not enough, there are several weak peaks of α-Zn_2SiO_4 remained is in XRD pattern. Compared to the XRD patterns, it is found that sample b (added SDS and cooled in air) and c (added SDS and quenched with water) have higher XRD diffraction intensity and sharper XRD peaks than that of sample a (no SDS and cooled in air). The intensification of XRD peaks would result in improved luminescent intensity due to the increase of crystallinity. This conclusion that samples b and c have higher photoluminescent intensity than sample a was easily obtained from the emission and excitation spectra.

The results of XRD can well explain the PL peaks at different positions shown in Fig. 1. Green luminescence centering at 525 nm corresponds to the α-phase Zn_2SiO_4, while yellow luminescence occurring at 575 nm comes from the β-Zn_2SiO_4 [23]. According to the above-mentioned opinion, the appearance of yellow luminescence is attributed to the higher crystal field in the β-Zn_2SiO_4 host.

To investigate the difference of intensity of photoluminescence in Fig. 1, the TEM images and corresponding SAED patterns were performed. Fig. 4 shows the images of the as-synthesized samples in different conditions. The micrographs of the as-synthesized sample a (no SDS and cooled in air) are shown in Figs. 4a–c. From the TEM (Fig. 4a) image it can be seen that the as-synthesized product is mainly composed of uniform rice-like particles with the average diameter of 150 nm and length of 300 nm. In fact, the rice-like nanoparticles consist of fine-sized nanorods. This is clearly revealed by magnified TEM images of a nanoparticle shown in Fig. 4b. The SAED pattern (Fig. 4c) obtained from this nanoparticle has a distortion dotted lattice, which reveals the crystalline nature of Mn-doped Zn_2SiO_4 nanoparticles.

Surfactant SDS plays a crucial role to obtain zinc silicate nanorods. It is clearly revealed by the TEM images shown in Fig. 4. In reactions b and c (see Figs. 4d and g), Zn_2SiO_4 nanorods can always be obtained if SDS is added. Fig. 4d shows a typical TEM image of the as-prepared Zn_2SiO_4 nanorods with the average diameter of 80 nm and length of several microns. Fig. 4e shows a representative Zn_2SiO_4 nanorod with high magnification. The SAED pattern (Fig. 4f) obtained from this individual nanorod has a highly symmetrical dotted lattice, which reveals the single-crystalline nature and further confirms the α-phase crystal structure of rod-like Zn_2SiO_4. Compared with sample b, nanorods of sample c have wide size distribution covering from 80 to 300 nm in diameter and several microns in length (Figs. 4g–h). This phenomenon may result from the inadequate Ostwald ripening growth process due to the quick cooling rate. The SAED pattern (Fig. 4i) obtained from a nanorod has a highly symmetrical dotted lattice, which demonstrates the single-crystalline nature and can be indexed to β-phase crystal structure of Zn_2SiO_4 nanorods. These results of SAED are in accord with that of XRD and further confirm the different

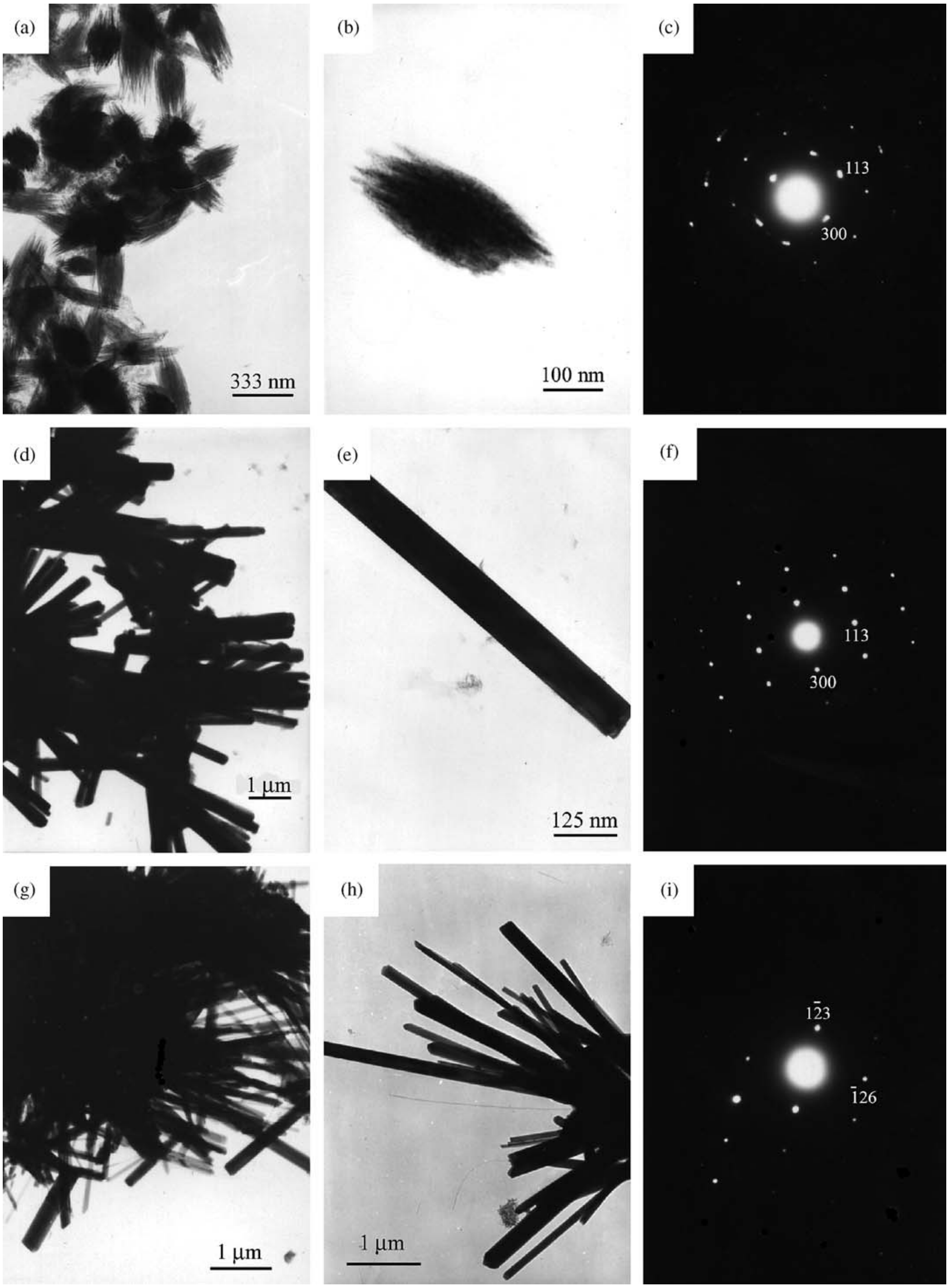

Fig. 4. Representative TEM image and the SAED pattern of synthesized samples at different conditions: (a–c) sample a—no SDS and cooled in air; (d–f) sample b—added SDS and cooled in air; (g–i) sample c—added SDS and quenched with water.

luminescence come from different crystal structure of Zn_2SiO_4.

Combining Fig. 1 with Fig. 4, it can be concluded that Zn_2SiO_4 nanorods have higher PL intensity than Zn_2SiO_4 nanoparticles. It is well known that nanosized materials have large surface area. The large surface area has the serious drawback in PL intensity due to the introduction of a large number of defects into the phosphor crystal. Defects have serious implications for luminescence materials as they provide non-radiative recombination routes for electrons and holes. In order for the material to be as efficient as possible, the number of electron/hole recombinations via optically active centers must be maximized. Therefore, the crystalline crystal is as important as the choice of host materials and the light-emitting center. If the host materials have high crystalline and little surface area, the proportion of surface-damaged region to undamaged bulk decreases. Higher PL intensity can be obtained as a result of the improved crystal quality [24]. Annealing treatment is an effective way to improve the emission intensities of phosphor due to low surface defects and improved crystallinity [25–27]. If the surface area is greatly reduced which results from the crystallite size increased, as a result the phosphor would show great improvement in the PL intensity [28]. Herein, the as-synthesized rice-like Zn_2SiO_4 nanoparticles are consisting of fine-sized nanorods. Compared with the large-sized Zn_2SiO_4 nanorods, nanoparticles have large surface area and low crystallinity. Therefore, a large number of electrons and holes in the excited state will return to ground state via non-radiative recombination routes. This is the reason that PL intensity of nanoparticles is lower than that of Zn_2SiO_4 nanorods.

4. Conclusions

In summary, Mn-doped Zn_2SiO_4 phosphors have been successfully synthesized via a low temperature hydrothermal route. The tunable PL properties were obtained through simple adjusting the experimental parameters. Apparently, two classes of samples have been obtained. One is characterized to the formation of α-phase zinc silicate nanoparticles and nanorods, that show green luminescence centering at 525 nm, and the other one is characterized as β-phase nanorods, showing yellow luminescence occurring at 575 nm. The as-synthesized Zn_2SiO_4 nanorods in the presence of surfactant SDS have higher PL intensity than Zn_2SiO_4 nanoparticles prepared in the absence of SDS. It is attributed to the low surface area and high crystallinity of Zn_2SiO_4 nanorods. Furthermore, this article provides a simple route to obtain Mn-doped Zn_2SiO_4 phosphors with different luminescence and PL intensity. The results may provide helpful guidance for the application of Mn-doped Zn_2SiO_4 phosphors.

Acknowledgements

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