A novel approach for preparation of Zn_2SiO_4:Tb nanoparticles by sol-gel-microwave heating

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Zn_2SiO_4:Tb nanoparticles were prepared by sol-gel-microwave heating for the first time. X-ray powder diffraction (XRD) analysis confirmed the formation of Zn_2SiO_4 in willemite structure. Field-emission scanning electron microscopy showed a narrow size distribution, small size (40–50 nm) and spherical shape of the particles. Energy dispersive spectroscopy result indicated that the ratio of Tb^{3+}/Zn^{2+} was in agreement with that of the feed. Photoluminescence measurement indicated that the phosphor emitted strong green light centered at 545 nm under UV light excitation. The excitation spectra confirmed the energy transfer from the host material to the Tb^{3+} ions. This is in favor of the effective green emission of Zn_2SiO_4:Tb nanoparticles. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

It is well known that Zn_2SiO_4 is a very good host material for rare earth ions and transition metal ions, with excellent luminescent properties in the blue, green and red spectra [1, 2]. Zn_2SiO_4 has been found applications in various devices because of its chemical stability and semiconductivity [3, 4]. Rare earth ions possess good luminescent characteristics with high color purity and high emission efficiency. Rare earths doped Zn_2SiO_4 phosphors are being applied in optical display and lighting application [5, 6]. They are also good candidates for field emission displays (FEDs). For high efficiency in FEDs, phosphors are required to have small size and spherical shape. With the development of the FEDs technology, more and more attentions are put onto nanomaterials because their significant properties are different from the bulk materials. Therefore, studies on rare earths doped Zn_2SiO_4 nanomaterials have attracted extensive interesting in recent years. Zhang and his coworkers prepared Zn_2SiO_4:Tb nanoparticles by sol-gel with traditional heating [7]. They used zinc acetate dehydrate [$Zn(AC)_2·2H_2O$], tetraethoxy-silicane [$(CH_3CH_2O)_4Si$, TEOS] and terbium acetate [$Tb(Ac)_3$] as starting materials.

Many investigations suggest that heating treatment is an important factor for controlling size and crystalline structure of the products. Microwave heating has been becoming a novel synthesis method and a rapidly developing research field [8]. Contrast to traditional heating, microwave heating consumes 10–100 times less energy and requires 10–200 times less time [9]. Microwave heating can achieve rapid and uniform heating of materials. Many applications of microwave heating have been reported in recent years [10–12]. In this paper, a novel approach for preparing Zn_2SiO_4:Tb nanoparticles by sol-gel-microwave was reported. Zn_2SiO_4:Tb nanoparticles was characterized by powder X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS) and photoluminescence measurements. The novel method showed the advantages of short reaction time, small size of product with a narrow size distribution and high purity.

2. Experimental
2.1. Preparation of ($Zn_{2−x}Tb_xSiO_4$ nanoparticles

All the reagents were of analytical grade. $Tb(NO_3)_3$ was freshly prepared by a reaction of Tb_4O_7 with dilute nitric acid and proper amount of H_2O_2. Firstly, $Zn(NO_3)_2·6H_2O$ was dissolved in de-ionized water and stoichiometric TEOS was dissolved in ethanol. Then, $Zn(NO_3)_2$ solution mixed with a varied ratio of as-prepared $Tb(NO_3)_3$ solution ($x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.06$) was dropped in TEOS solution at a rate of 20 drop/min with vigorously stirring. Finally, a proper amount of 0.1 mol/L HNO_3 was applied as the catalyst for the hydrolysis of TEOS. A transparent sol was obtained after 3 h stirring, and 2 or 3 days later a transparent gel was attained. Dry gel precursor was prepared by baking the gel at 110°C for 1 h. The dry gel precursor was placed in a corundum crucible inside a large uncover tile crucible. SiC was filled as the heating medium between the corundum and tile crucible. Then the tile crucible was placed in a microwave

oven (Model Ms-Z588SDTM, LG Company, Korea) with a microwave frequency of 2450 MHz. A series of calcination experiments with varying heating time and microwave power output based on orthogonal design method were done to optimize the technical conditions of microwave heating for obtaining $(Zn_{2-x}Tb_x)SiO_4$ nanoparticles.

2.2. Apparatuses and measurements

Powder X-ray diffraction (XRD) (D/max—IIIA diffratometer, RIGAKU Corporation of Japan. 35 kV and 25 mA, Cu Kα = 1.5406 Å, Rigaku/Dmax-IIIA) was used for crystal phase identification and estimation of the crystal size.

The morphology and size of the calcined particles were observed by field-emission scanning electron microscopy (FE-SEM, JSM-6330F, JEOL Corporation of Japan). Platinum power was sprayed onto the sample surface before FE-SEM observation.

Doped terbium concentration of the $(Zn_{2-x}Tb_x)SiO_4$ samples was measured from Kα lines of Tb element by energy disperse spectroscopy (EDS) installed in a Hitachi S-520 scanning electron microscope.

Thermogravimetric analysis (TGA) of the dry gel was carried out on a thermogravimetric analyzer (NET-ZSCH TG 209, Germany) in air (20.00 ml/min) in a range of 23–930°C with a calefactive rate of 10.0°C/min. DSC curve of the Zn_2SiO_4 power gel was measured on a Differential Scanning Catorimeter (DSC-1700, Perkin-Elmer Corporation of America) in a range of 23–930°C with a scan rate of 10°C/min in air (45.00 ml/min).

Photoluminescence (PL) and PL excitation (PLE) spectra were taken on a Hitachi F-4500 fluorescence spectrophotometer (Japan) with both excitation and emission slits of 5 nm, a scan rate of 240 nm/min, a PMT at 700 V and a 150 W Xenon lamp as an excitation source at room temperature.

The lifetimes of the phosphors were taken on an FLS920 luminescence spectrometer.

3. Results and discussion

Fig. 1 is the TG-DTG curves of the precursor sample prepared by sol-gel. The TG curve showed remarkable weight-loss at 77.6°C and 109.6°C due to loss of H_2O and CH_3CH_2OH respectively. Because of the oxidization and evaporation of OH and the organic groups, there was a weight-loss in the curve at 333.6°C. At higher temperature, smooth weight-loss was attributed to the remove of the OH and NO_3. When the temperature was above 850°C, the weight-loss was unnoticeable. The result was consistent with the DSC curve as shown in Fig. 2. When the temperature was as high as 850°C, the DSC curve became a beeline because of the variety of specific heat at high temperature. The result revealed that good crystalline product can form at 850°C, which was confirmed by further calcination experiments.

The effects of the amount of ethanol and de-ionized water, the microwave power and the heating time on
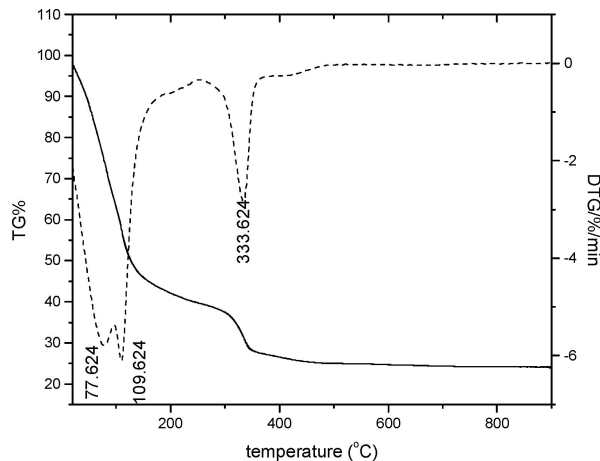
Figure 1 TG-DTA curves for the precursor gel (gel dried at 110°C for 1 h).
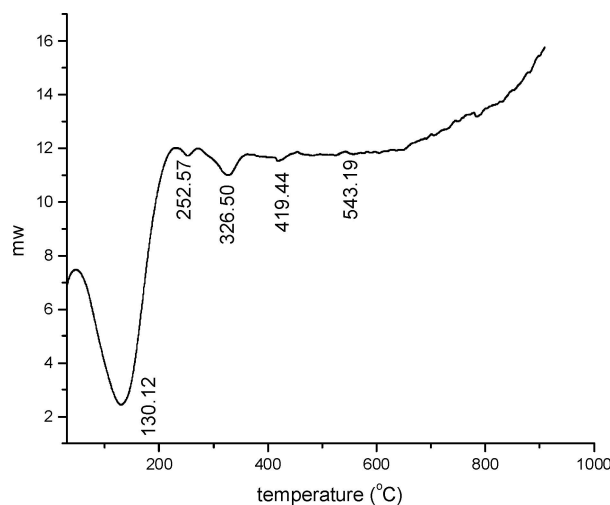
Figure 2 DSC curve for the precursor (gel dried at 110°C for 1 h).

the size and the luminescence properties of formed particles were investigated by orthogonal design experiments. The results showed that the amount of ethanol and de-ionized water played a small role while the microwave power and the heating time affected the size and the photoluminescence in a big degree. The optimum molar ratio of TEOS:ethanol:de-ionized was 1:5:12. The optimum microwave-heating conditions were fixed to 800 W and 15 min.

Fig. 3 showed XRD patterns of the samples heated by microwave oven for different time of 10, 12 and 15 min, respectively. The samples heated for 10 and 12 min had poor crystalline state, while good crystalline particles were obtained after heating for 15 min. The peak positions agree well with those of the standard pattern reported by the Joint Committee on Powder Diffraction Standards (JCPDS, 8-492) for Zn_2SiO_4 in willemite structure. The diffraction peaks corresponding to (110), (300), (220), (113), (140), (223), (333), (006), (630) and (713) indicated that the product possesses a pure phase in rhombohedral structure. The average particle size of the powder prepared by sol-gel microwave heating was calculated to be 47 nm according to the Debye-Scherrer equation [13]:
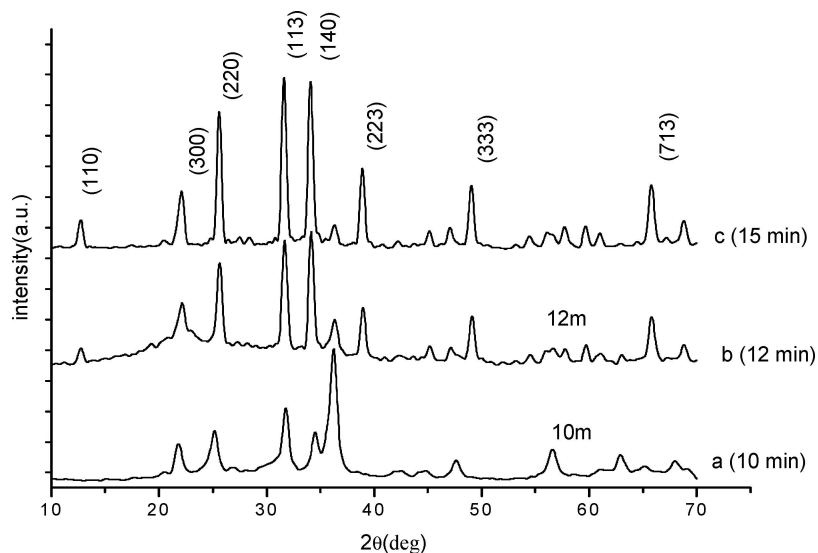
$$D = k\lambda/\beta(2\theta)\cos\theta,$$

Figure 3 XRD patterns for Zn_2SiO_4:Tb nanoparticles prepared by sol-gel-microwave heating (a) 10, (b) 12, and (c) 15 min.

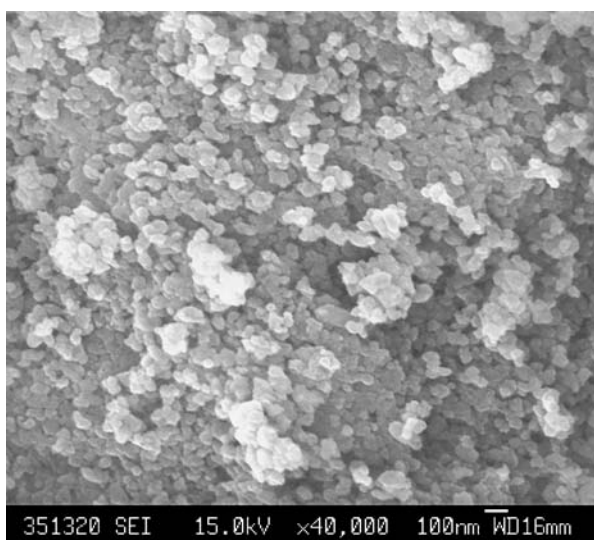*Figure 4* FE-SEM images of Zn_2SiO_4:Tb nanoparticles prepared by sol-gel-microwave heating (800 W, 15 min).

Figure 5 Excited spectra for Zn_2SiO_4:Tb nanoparticles prepared by sol-gel-microwave heating (λ_{em} = 545 nm, 800 W, 15 min).

where λ is the wavelength of the X-ray (1.5406 Å), $\beta(2\theta)$ is the width of the pure diffraction profile in radians, 2θ is the diffraction angle, D is the average diameter of the crystallite, and k is a constant ($k = 0.89$). FE-SEM image (Fig. 4) showed the morphology was spherical-like shape and the size was uniform for the Zn_2SiO_4:Tb nanoparticles prepared by sol-gel-microwave heating. The particle size is 40–50 nm, which is accordant with the calculation result. Contrarily, Zn_2SiO_4:Tb sample prepared by traditional heating in a high-temperature oven at 850°C for 1 h and 20 min showed serious agglomeration.

An interesting phenomenon was found in the excitation spectra of $(Zn_{2-x}Tb_x)SiO_4$ nanoparticles. Fig. 5 shows the excitation spectra of Tb-doped Zn_2SiO_4 nanoparticles with different concentration varied from $x = 0.01$ to $x = 0.06$ monitored at 545 nm. The excitation spectra were different from that of Zn_2SiO_4:Tb nanoparticles prepared by Zhang and his coworkers [7]. The excitation spectra of $(Zn_{2-x}Tb_x)SiO_4$ nanoparticles with $x = 0.01$, $x = 0.02$, $x = 0.03$ show two peaks
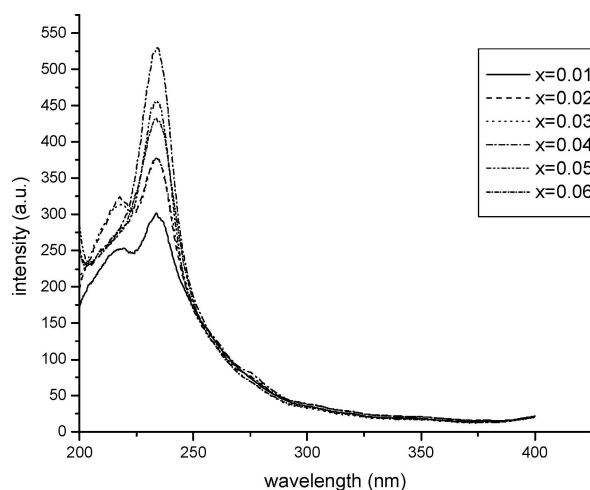
centered at 216 and 234 nm respectively. While the excitation spectra of $(Zn_{2-x}Tb_x)SiO_4$ with $x = 0.04$, $x = 0.05$, $x = 0.06$ have no obvious excitation band at 216 nm. We suggested the excitation band centered at 216 nm was attributed to UV-absorption of Zn_2SiO_4. In bulk Zn_2SiO_4, Zn^{2+}, which is a d^{10} ion and coordinated to four oxygen atoms, shows an intense and broad absorption in the UV region [14–16]. The absorption edge of Zn_2SiO_4 is 225 nm (5.5 eV). Furthermore, the absorption of Zn_2SiO_4 becomes relativity intense in nanomaterials. Although the exact nature of the UV-absorption band is not fully understood, most likely the band is due to a charge transfer transition from the $2p$ orbital of oxygen to an antibonding orbital partly localized on the d^{10} ion of Zn^{2+} and partly on the oxygen itself [14]. UV energy absorbed by Zn_2SiO_4 was transferred to Tb^{3+} ions, and favored the green emission of Zn_2SiO_4:Tb nanoparticles. The phosphors have weak green emission when excited by 216 nm. This confirmed the energy transfer to the Tb^{3+} ions. The excitation band centered at 234 nm originates from a $4f^8$–$4f^75d^1$ transition. At the low Tb^{3+}-doped concentration, the energy transition is relatively strong, so the
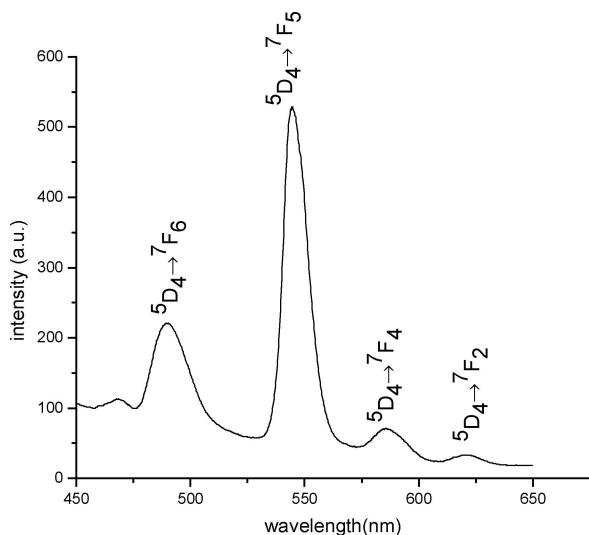
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Figure 6 PL spectrum for 4% Zn_2SiO_4:Tb nanoparticles prepared by sol-gel-microwave heating (800 W, 15 min, $\lambda_{ex} = 234$ nm).

excitation band of the host absorbed was found. As we all know, the *f–d* transition is a permitted transition. As the doped-Tb^{3+} concentration increased, the excitation band from the *f–d* transition is so strong that the excitation band centered at 216 can not be found. We can see that there is energy transition in Zn_2SiO_4:Tb phosphor. This is in favor of the effective green emission of Zn_2SiO_4:Tb nanoparticles.

Fig. 6 is the PL spectrum for $(Zn_{2-x}Tb_x)SiO_4$ nanoparticles. The phosphor showed an intensely green emission centered at 545 nm when excited by 234 nm. The PL intensity increased with the doped-Tb^{3+} concentration up to $x = 0.04$. When the concentration of Tb^{3+} increased above $x = 0.04$, the emission intensity became weaker without change in emission wavelength. The ratios of Tb to Si were determined by EDS, which were in good agreement with the feed. The four main emission peaks for $(Zn_{2-x}Tb_x)SiO_4$ were originated from the $^5D_4 \rightarrow {}^7F_j$ transitions of Tb^{3+} ions, located at 490 nm ($j = 6$), 545 nm ($j = 5$), 586 nm ($j = 4$), 621 nm ($j = 2$), and the green emission of $^5D_4 \rightarrow {}^7F_5$ was obviously predominant.
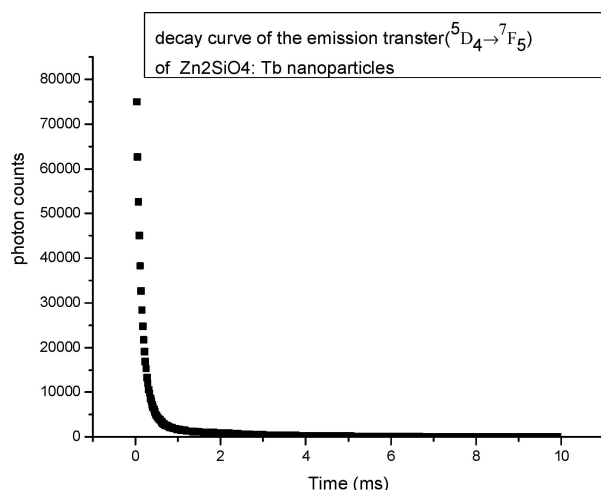

Figure 7 Decay kinetics of Tb^{3+} emissions in $(Zn_{2-x}Tb_x)SiO_4$ ($x = 0.04$) nanoparticles ($\lambda_{ex} = 234$ nm, $\lambda_{em} = 543$ nm).

Fig. 7 present the decay kinetics of Tb^{3+} emissions in $(Zn_{1.96}Tb_{0.4})SiO_4$ nanoparticles. The luminescence decay lifetime of 543 nm exhibits a bi-exponential fit when excited at 234 nm with $\tau_1 = 1.2934$ ms, $\tau_2 = 0.1195$ ms.

4. Conclusions

Terbium-doped Zn_2SiO_4 nanoparticles were successfully prepared by sol-gel-microwave method with a narrow size distribution, spherical shape and high purity. PL measurement showed intensely green emission from $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} ions in Zn_2SiO_4 :Tb^{3+} nanoparticles. The excitation bands were attributed to the energy transfer from the host material of Zn_2SiO_4 to Tb^{3+} ions. It is a good candidate for green phosphor in FEDs.

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