

Novel silicate sources synthesized nanophosphors Zn_2SiO_4 : Eu^{3+} and luminescent property

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Six kinds of different silane coupling agent was used as silicate sources to prepare the luminescent species Zn_2SiO_4 : Eu^{3+} with 20 – 30 nm size by sol-gel method. Some samples present novel micro morphology. All the nanometer materials exhibit strong red emission at 610 nm. Results indicate the silicate sources have influence on the micro morphology and luminescence intensity of the nanomaterials. The results show the potential for lowering the thermolysis temperature by changing the silicate sources.

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1. Introduction

Nano-sized materials have been studied vigorously over the past years because their significant optical and electronic properties are different from their bulk form. The dynamical properties of these new nanostructured solid state materials are expected to differ significantly from those of regular crystals and glasses. The modified phonon spectrum and effects of confinement in nanoparticles as well as the effects of disorder-induced two-level systems may greatly influence the optical properties of impurity ions [1]. Novel luminescent properties were found in materials with nano-size: the emission line broadens, the lifetime changes, the spectra shift and the intensity ratio of the magnetic dipole transition to the electric dipole transition change [2, 3, and 4]. This indicates nano-size material is a candidate technology for high-resolution imaging [5] and luminescent devices. More and more new application in the optical material began to attach importance to the smaller size, narrow size distribution, and regular morphology.

Among various host for luminescent material, willemite Zn_2SiO_4 has been identified as a very suitable host matrix for many rare earth and transition metal dopant ions due to their high luminescence efficiency and chemical stability, and becomes the subject of active research in recent years. Zn_2SiO_4 doped with Eu^{3+} , Mn^{2+} (Tb^{3+}), or Ce^{3+} covers the red, green, and blue regions of the visible spectrum, respectively [6-9]. As for applications, Zinc orthosilicate (willemite, Zn_2SiO_4 , trigonal crystalline system, Rh3 space group 3) doped with divalent manganese ions is commercially used as a green phosphor [10]. Zn_2SiO_4 can be found useful in various devices such as ray tubes and electroluminescence devices [11,12] because of its chemical stability and semiconducting properties [13, 14]. However, to our best

knowledge, most of the silicate host materials were synthesized by employing the tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS). There have been a few studies highlighting in changing of the silicate source [15].

Traditional synthesis methods of luminescent materials were mainly focused on the solid-state reaction and a sputtering technique [16, 17 and 18]. However, the conventional solid state method, because of the requirement of high calcinations temperatures and long reaction times (the calcinations temperature for the synthesis of Zn_2SiO_4 is around 1300 °C [19]), leads to the aggregation of the resulting particles that exhibit poor morphology and wide size distribution [20]. We focus on a novel soft chemistry method; the sol-gel method approach, which is based on hydrolysis/polycondensation reactions, exhibits its unique characteristics, namely, convenience, low temperature, and versatility [21-25]. For most applications, it is essential for RE doped sol-gel materials to have high-fluorescence quantum yields [26].

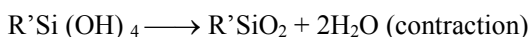
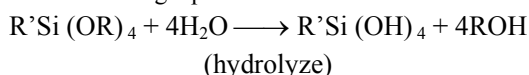
Hybrid polymeric films have been prepared and the luminescence of Tb and Eu has been studied in previous papers [27,28].

The goals of the current study are to consider the effect of eight different kinds of silicate sources on the spectroscopic properties of Zn_2SiO_4 : Eu^{3+} . The six different silicate sources will be explained in detail in the experimental part. Because of large distinctness in the hydrolyzing speed, polymerized form of different silicate sources, the products exhibit various configuration and character. The advantages of some silicate sources: low-cost, non-toxicity, and short reaction time, may make them candidate materials for the synthesis of rare earth silicates.

2. Experimental

Synthesis. The starting materials Eu_2O_3 used in these

studies were at least analytical grade. Rare earth nitrates were prepared from the oxides by treating concentrated nitric acid. The synthesis of $\text{Zn}_2\text{SiO}_4\text{:Eu}^{3+}$ precursors were described in the following: appropriate amounts of $\text{Eu}(\text{NO}_3)_3$ and zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{AC})_2$) aqueous solutions were added and mixed homogeneously. The pH value was adjusted by HNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ to about 5. And then the silicon sources {3-aminopropyltriethoxysilane [$\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$] (APES), 3-Glycidoxypentyl-trimethoxysilane [$\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$] (GPMS), N-2-aminoethyl-3-aminopropyl-diethoxysilane [$\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2$] (AEAPMMS), N-2-aminoethyl-3-aminopropyl-trimethoxysilane [$\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$] (AEAPMS), 3-aminopropyl-methyldiethoxysilane [$\text{NH}_2(\text{CH}_2)_3\text{SiCH}_3(\text{OC}_2\text{H}_5)_2$] (APMES) and N-2-aminoethyl-3-aminopropyl-triethoxysilane [$\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$] (AEAPES)} were added into the above solutions to form a gel. Finally, by slow evaporation of the solvent, the precursors were obtained and dried at about 80 °C. At last the precursors were calcinations at 900 °C for about 4 hours. The typical scheme of the sol-gel process can be shown as below:



In the sol system, when there exist enough Si-O-Si, the gel system with lots of articulate appeared in microcom. Then the particulates connected further, the gel system formed. The speed and the configuration are influenced by pH value, temperature, solvent and the quantity of water. In order to make comparison, material using tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) as silicate source was synthesized by the same method.

Measurements and apparatus

The production was characterized by means of X-ray diffraction (XRD, 40 kV and 40 mA, $\text{CuK}\alpha$, Bruck D8-Advance) and scanning electronic microscope (SEM, Philips XL-30). A Netzsch thermoanalyzer, STA 409, was used for simultaneous thermal analysis combining the thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) with a heating rate of 10 Kmin^{-1} . Excitation spectra were determined by Perkin-Elmer LS-55 model fluorophotometer (excitation wavelength = 613 nm, scan rate = 1000 nm/s, both excitation and emission slit width are 5.0 nm). In order to avoid the influence of multiple frequency, we recorded the excitation spectra in the two regions 220 – 280 nm and 320 – 450 nm.

3. Results and discussion

Fig. 1 gives the TG/DSC charts of the Zn_2SiO_4 precursor dry gel carried out in static air. All the curves present similar property except the sample using GPMS.

We choose the one by APES as an example (Fig. 1A). From room temperature to around 140 °C, there is a continuum weight loss of about 10% and accompanied by an endothermic peak at about 85 °C which is due to the evaporation of adsorbed water. At about 220 °C, a sudden weight loss of 35% appear which is attributed to decompose and burning of some organic matter like $-\text{NH}_2$. It produced a mass of heat at the moment which gives a high temperature to the precursor. With the rising of temperature, the carbon began to burning and brought an exothermic peak at around 400 °C. After 500 °C, there is no obvious weight loss. The sample by GPMS show a different character in the TG/DSC curve (Fig. 1B), it did not have an abrupt weight loss and exothermic peak but a durative process. It may be another reason to form the homogeneous configuration.

X-ray diffraction grams obtained for all samples are represented in Fig. 1a. All the diffraction peaks match very well with the standard values from the Joint Committee on Powder Diffraction Standards (JCPDS) data card (No. 37-1485), which was indexed in the hexagonal system with centrosymmetric space group $\text{R}\bar{3}[148]$. The average crystallite size was estimated from the full width at half maximum of the diffraction peak by the Sherrer equation [29,30]. When the strongest three (220) (113) (410) diffraction peaks in Fig. 1 is chosen for the calculation, an average crystallite size of 20 - 30 nm is obtained. Fig. 1b is the XRD of product by TEOS. Besides the Zn_2SiO_4 phase (JCPDS 37-1485), the main phase ZnO (JCPDS 89-1397) was appeared. The result indicates that the changing of silicate sources may lower the phase form temperature of Zn_2SiO_4 . The silane coupling agents contains different organic groups especially those with carbon like alkyl. During the thermolysis process, the organic groups can serve as a fuel and the quenching temperature can be reduced.

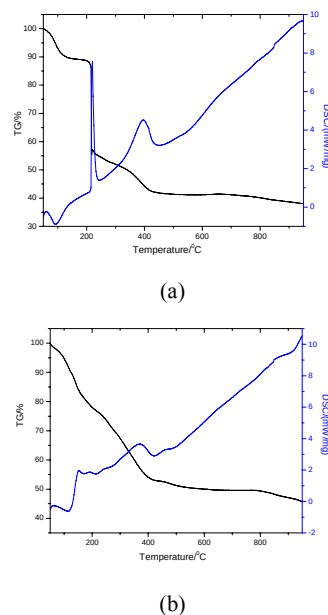
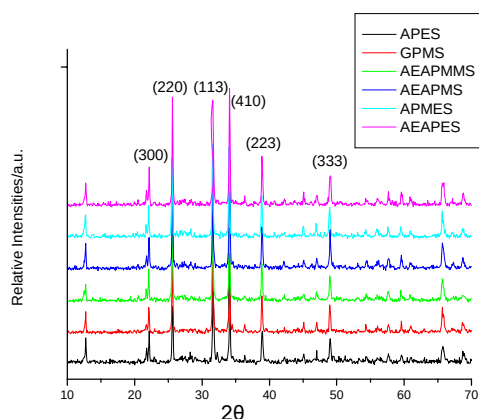
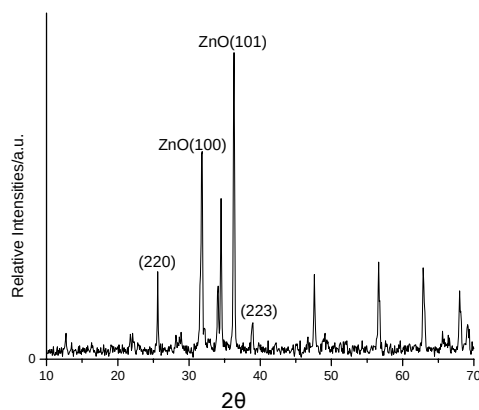


Fig. 1. TG/DSC analysis of $\text{Zn}_2\text{SiO}_4\text{:Eu}^{3+}$ by different silicon sources: (A) APES, (B) GPMS.



(a)

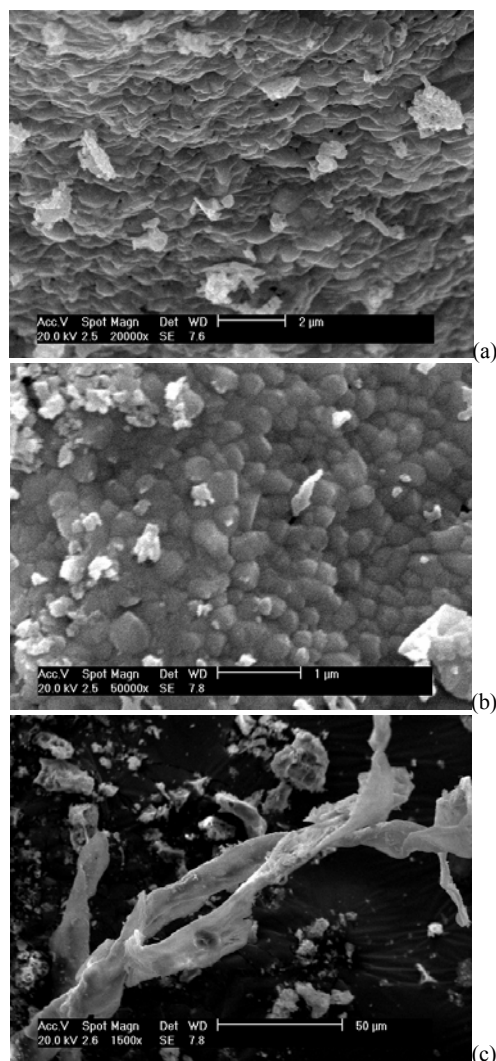
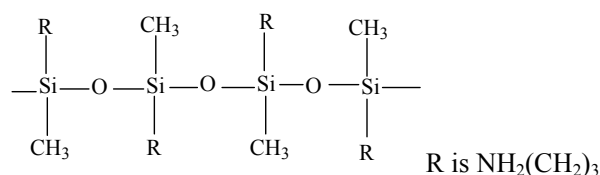


(b)

Fig. 2. XRD pattern of $\text{Zn}_2\text{SiO}_4: \text{Eu}^{3+}$ by different silicate sources: (A) silane coupling agents, (B) TEOS.

We further measured the scanning electric microscope (SEM) of nanometer $\text{Zn}_2\text{SiO}_4: \text{Eu}^{3+}$ samples (as shown in Fig. 3). It can be predicted approximately the crystal particle is in the size less than 100 nm, which takes agreement with the data from the XRD estimation. The organic groups in the silane coupling agents were able to interact with the metal ions and function with each other. Sometimes, the organic groups can be regarded as dispersing medium, limiting the agglomeration of particles and control the size of particles. During the reaction, many gases, such as CO_2 , N_2 , NO_2 and H_2O , as well as a large amount of in situ generated heat, were released in a short period of time before the process terminated with white, foamy and crisp products. The one using GPMS have the most homogeneous configuration of regular granules (Fig. 3B). It may contribute to its ether group without polarity. Furthermore we find that the silicate sources with -NHX exhibit an interpenetrating network structures and the shape of the granules is not very regular. The pair of AEAPMS and AEAPES with similar structure

is a good example. It was supposed that the active -NHX is easy to function with other groups. When it has bonds in all direction, the interpenetrating network structures would be simple to explain. An interesting phenomenon was found in the sample synthesized by APMES where many long chains were found in the SEM (Fig. 3C). Considering the frame of APMES the material contains only two (OCH_3) and other two functional groups are (CH_3) , $\text{NH}_2(\text{CH}_2)_3$. For the space number it is conjectured that the APMES would give a hydrolysis/polycondensation reaction in the following way:



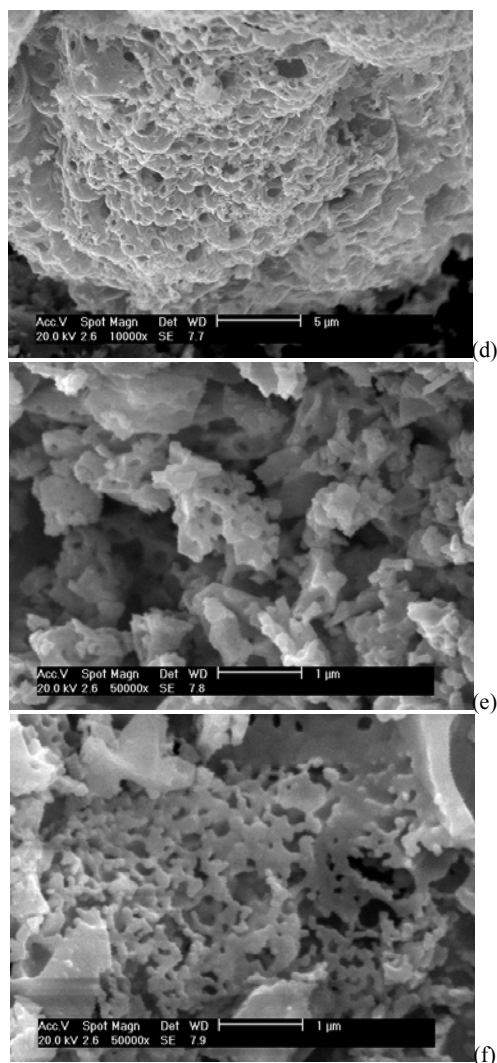


Fig. 3. SEM microscope of $\text{Zn}_2\text{SiO}_4: \text{Eu}^{3+}$ by different silicon sources: (A) APES, (B) GPMS, (C) APMES, (D) AEAPMMS (E) AEAPMS, (F) AEAPES.

However, the phenomenon wasn't as obvious in the AEAPMMS which also have two $-\text{OR}$. It is also due to the space cumber. In the AEAPMMS, besides the two $-\text{OR}$ the other two groups connect with Si are $-\text{CH}_3$ and $-\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3$. Compared with $-\text{NH}_2(\text{CH}_2)_3$, $-\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3$ it is much bigger There isn't enough space for the group if AEAPMMS hydrolysis/polycondensation follows the same mode as APMES. So the most appropriate way is to connect one by one to form a hollow ring. (Fig. 3D) This will also explain the sandwich. It can only growth in one surface.

The excitation and emission spectra at room temperature of $\text{Zn}_2\text{SiO}_4: \text{Eu}^{3+}$ samples prepared by different silicate sources are represented in Fig. 4. Because there is no obvious peak in the range of 220 – 280 nm, the excitation spectra in this range was not given. The excitation spectra (320 – 450 nm) measured fixing the

highest intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ Eu^{3+} relaxation transition (613 nm) in Fig. 4A, show the group of Eu^{3+} excitation transitions assigned to $^7\text{F}_0 \rightarrow ^5\text{D}_3$, 4, $^5\text{L}_6$ and $^5\text{G}_1$. The corresponding emission spectra using the 393 nm excitation $^7\text{F} \rightarrow ^5\text{L}_6$ transition, shown in Fig. 4B, is a set of relaxation transitions $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) in the red region attributed to the Eu^{3+} in low-symmetry sites. Luminescence from higher excited states, such as $^5\text{D}_1$, is not detected indicating very efficient nonradiative relaxation to the $^5\text{D}_0$ level. The strongest emission peaks both are located at 610 nm, corresponding to the typical hypersensitive transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ for Eu^{3+} ion, which is forbidden f-f intraconfigurational transition. It is allowed in this case, as the europium does not occupy a center of symmetry in Y. The minor emission component in the orange region around 590 nm due to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole transition is structurally independent. For this reason, this transition can be used as an internal stand to gain some idea of the relative transition strengths of the other transitions of Eu^{3+} [31]. Due to weaker interaction Eu^{3+} and O^{2-} ions in Zn_2SiO_4 doped with Eu^{3+} , no level split can be caused by the crystal field and no obvious split of Eu^{3+} emission bands has been observed.

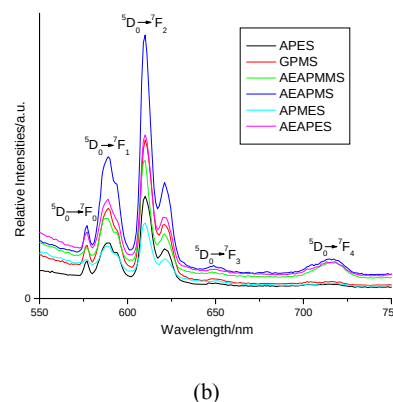
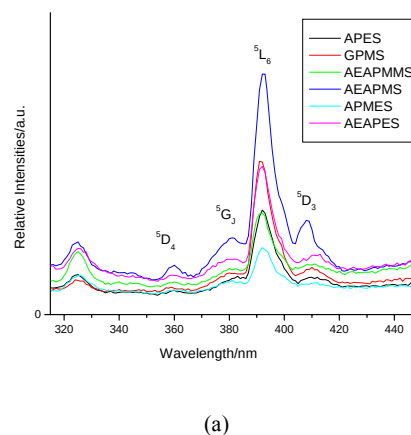


Fig. 4. (A) Comparison of excitation spectra of $\text{Zn}_2\text{SiO}_4: \text{Eu}^{3+}$ by different silicon sources in the range of 310 – 450 nm, (B) Comparison of emission spectra of $\text{Zn}_2\text{SiO}_4: \text{Eu}^{3+}$ by different silicon sources.

If one compares the relative intensities for different silicon sources, the excitation and emission spectra gave the similar information. The sample using AEAPMS seems to be superior to others.

4. Conclusions

In summary, the synthesis of $\text{Zn}_2\text{SiO}_4: \text{Eu}^{3+}$ nanophosphors were achieved under 900 °C by introducing different silane coupling agents as silicate source. The structures have been investigated to be composed of nanometer-size grains of 20 – 30 nm with a willemite structure ($\alpha\text{-Zn}_2\text{SiO}_4$). The photoluminescence properties show both of them exhibit the characteristic fluorescence $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) of Eu^{3+} ion and the strongest one is the red emission at 610 nm. Comparing with the one synthesis by TEOS, all the samples show the potential for lowering the thermolysis temperature. Some of the nanophosphors present regular micro morphology, which indicates they are candidates for the synthesis of nanometer silicon based materials.

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