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Combustion synthesis and photoluminescence of $Sr_2MgSi_2O_7$:Eu,Dy long lasting phosphor nanoparticles

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Abstract

SiO_2 and $Si(OC_2H_5)_4$ were employed as the raw materials to synthesize blue long afterglow phosphor $Sr_2MgSi_2O_7$:Eu,Dy via a combustion process with ultrasonic dispersing technique, respectively. The crystallization, particle sizes and luminescence properties of the samples have been investigated systematically by using powder X-ray diffraction, transmission electron microscopy, luminescence spectrophotometer and brightness meter. Compared with the phosphor obtained by employing SiO_2 as starting material, the phosphor powder prepared by using $Si(OC_2H_5)_4$ has purer $Sr_2MgSi_2O_7$ phase, smaller particle size, and shorter wavelength of main peaks of excitation and emission spectra. Nanoparticles can be obtained by using $Si(OC_2H_5)_4$ as starting material. The afterglow properties of the phosphors were also studied in this article.

Keywords: Combustion; Alkaline earth silicate; Phosphor; Luminescence

1. Introduction

Recently, alkaline earth silicates with high brightness have attracted much attention for the application in long lasting phosphors [1–6]; they are characteristic with chemical and physical stability, especially an excellent water-resistant property. Barry [7–9] reported the luminescent properties of many silicate phosphors. The peak positions of different silicate hosts in the emission spectra depend strongly on the nature of the Eu^{2+} surroundings. Xiao et al. [10,11] synthesized $Sr_2MgSi_2O_7$:Eu,Dy phosphor, and its afterglow lasts more than 5 h. However, most of silicate-based long afterglow materials were synthesized traditionally by solid-state reaction, which demands high temperature and long time. In addition, the grain size of phosphor powders is in several tens of micrometers and the phosphor powders must be ground in order to obtain small particles. These processes easily introduce additional defects and greatly reduce luminescence efficiency [12]. With the development of nano-technology, ultrafine particles have been recognized to hold tremendous potential in many applications and are also required in the area of phosphors. Monodispersed, small and spherical particles are required for their application in field emission display (FED) [13] while coarse particles normally produce much more light scattering and increase the consumption of phosphors [14].

Combustion synthesis gives a low-density mass reducible to quite fine particles with almost no effort. The processing method may avoid the use of H_2 atmosphere during the thermal treatments, since the organic matter generated during the combustion of itself produces the reducing atmosphere [15]. However, the difficulty to synthesize luminescent materials of silicate host by combustion method resides in the fact that silica is insoluble in water and in majority of acids.

In this study, due to SiO_2 insolubility in water, $Si(OC_2H_5)_4$ was employed as raw material to prepare $Sr_2MgSi_2O_7$:Eu,Dy (hereafter denoted SMS-SOC) nanoparticles by combustion method and the phosphor was compared with that obtained by using SiO_2 (hereafter denoted SMS-SO). The lattice structure, morphology, photoluminescence and afterglow characteristics were examined. The effects of $Si(OC_2H_5)_4$ on the luminescence properties of $Sr_2MgSi_2O_7$:Eu,Dy phosphor were also investigated.

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2. Experimental procedure

$Sr(NO_3)_2{\cdot}4H_2O$, $Mg(NO_3)_2{\cdot}4H_2O$, SiO_2, $Si(OC_2H_5)_4$, Eu_2O_3, Dy_2O_3, H_3BO_3, and $CO(NH_2)_2$, all in analytical grade, were used as the starting materials in the experiment. The raw materials were weighed as the nominal composition $Sr_{1.95}MgSi_2O_7$:$Eu_{0.05}$,$Dy_{0.05}$. The stoichiometric mixture of reagents (without SiO_2 or $Si(OC_2H_5)_4$) was dissolved in a certain amount of deionized water to obtain a transparent solution. Eu^{2+} and Dy^{3+} were introduced in the form of $Eu(NO_3)_3$, $Dy(NO_3)_3$ solution by dissolving Eu_2O_3, Dy_2O_3 into HNO_3 solution. $Si(OC_2H_5)_4$ and appropriate amount of ethanol was added slowly into the homogeneous solution and made it mushy with ultrasonic dispersing technique (SiO_2 was added slowly into when the solution was heated to boil, whereafter ultrasonic dispersing for about 15 min) and the mixture was transferred to a muffle furnace preheated to 600–800 °C. Initially, the mixture boiled, underwent dehydration, followed by decomposition with the evolution of large amounts of gases (oxides of carbon, nitrogen and ammonia). Then, spontaneous ignition occurred and underwent smouldering combustion with enormous swelling, producing white foamy and voluminous ash. The entire process lasted for 3–5 min. The product SMS-SOC was more voluminous and more easily milled than SMS-SO.

The synthesized products were characterized by X-ray diffraction (XRD) using a Bruker D8 (Bruker Co., German) X-ray diffractometer with graphite monochromatized Cu Kα irradiation ($\lambda = 1.5406$ Å). The morphology was taken with a Tecnai G20 (FEI Co., Holland) transition electron microscope (TEM). Excitation and emission spectra were measured on a Perkin-Elmer Ls-55 (Perkin-Elmer Co., USA) fluorescence spectrophotometer. The decay curve of persistent luminescence was measured by the ST-86LA (China) brightness meter.

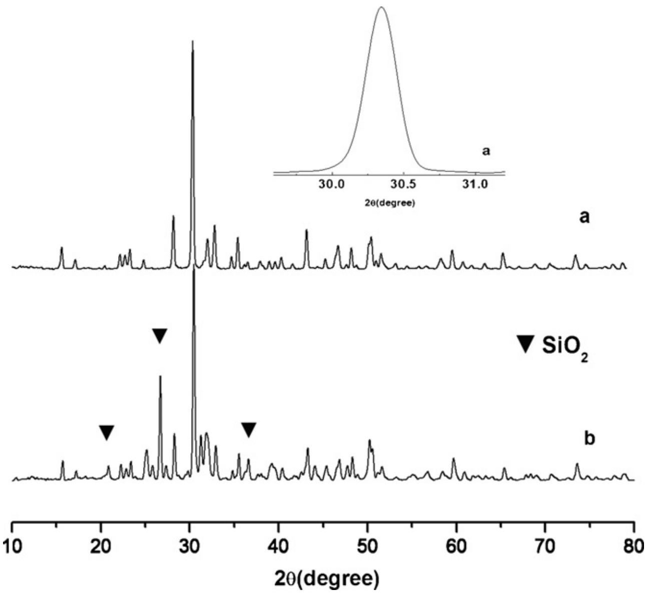

Fig. 1. XRD patterns of $Sr_2MgSi_2O_7$:Eu,Dy prepared by (a) $Si(OC_2H_5)_4$ and (b) SiO_2 source.

3. Results and discussion

3.1. Phase composition of the obtained phosphors

The XRD patterns of SMS-SOC (Fig. 1a) and SMS-SO (Fig. 1b) are shown in Fig. 1. The positions and the intensity of diffraction peaks of the powder SMS-SOC are consistent with the JCPDS card No. 75-1736. $Sr_2MgSi_2O_7$ crystallizes in the tetragonal crystal system in space group $P42_1m$ (No. 113) with cell parameters $a = b = 7.995$ Å and $c = 5.1521$ Å. Nearly no other phase is observed. According to the Scherrer equation, the average crystallite size of SMS-SOC phosphor calculated by

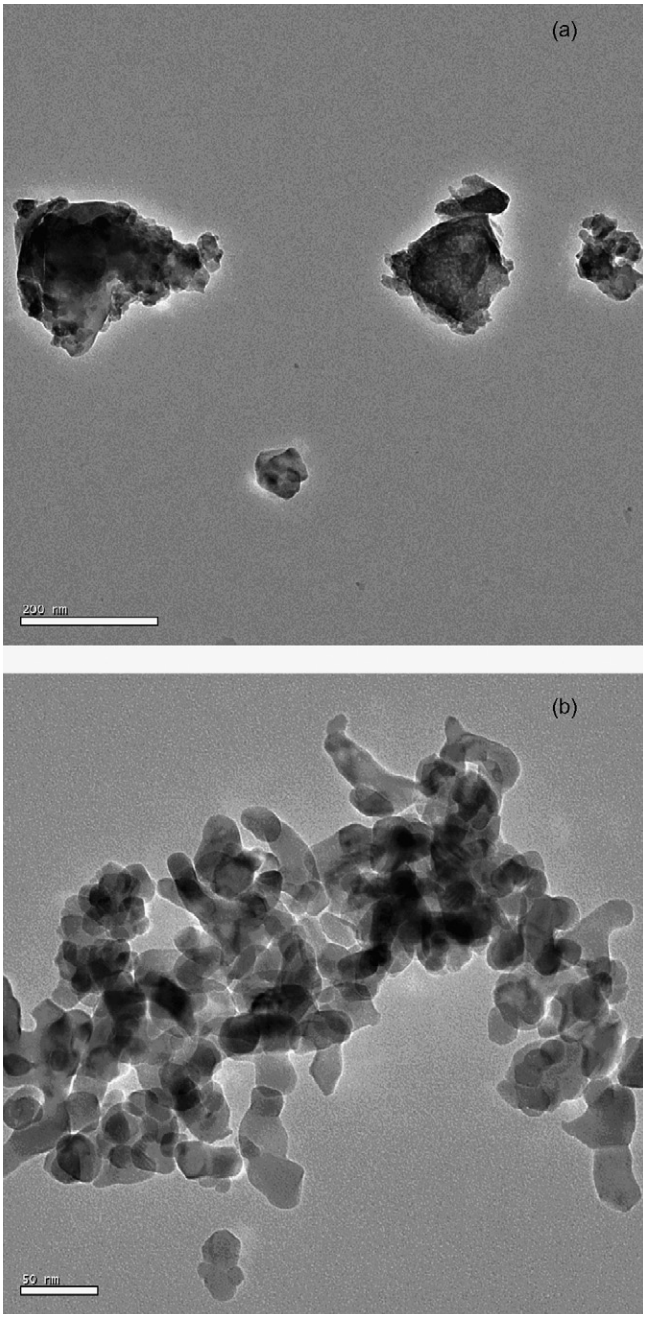

Fig. 2. TEM micrograph of $Sr_2MgSi_2O_7$:Eu,Dy prepared by (a) SiO_2 and (b) $Si(OC_2H_5)_4$ source.

using the most intense reflection at $2\theta = 30.3425°$ is 14.1 nm. However, the pattern of SMS-SO shows a small quantity of quartz phase. The reason may be that it is difficult for SiO_2 to be dissolved in water to form homogeneous solution with other substance. Because of short time and drastic reaction, small quantities of SiO_2 do not enter into the host crystal lattice.

3.2. Morphology of phosphors

Fig. 2a and b show the TEM micrographs of the strontium magnesium silicate, namely SMS-SO and SMS-SOC. Particle size of the SMS-SOC is smaller and more homogeneous than that of the SMS-SO phosphor. Fig. 2b shows that the morphology of SMS-SOC is homogeneous and the average size of particles is about 20 nm. This value is in accordance with that obtained from XRD measurements. The prepared process which obtain SMS-SOC phosphor is similar to sol–gel route, so it is easier to obtain small particle sizes with high surface area. Furthermore, for the preparation of SMS-SO phosphor, the insoluble SiO_2 suspend in the solution. In case of combustion synthesis, instantaneous and in situ very high temperature, combined with release of large volume of volatiles from mixture is easy to result in aggregation.

3.3. Luminescence properties of phosphors

Figs. 3 and 4 show the excitation and emission spectra of SMS-SOC and SMS-SO at room temperature, respectively. Both of them show two broad bands in the excitation spectra and only main peak in the emission spectra. It is observed that the main peaks of excitation and emission spectra of nanometer phosphor shift to shorter wavelength (from 350 to 335 and 399 to 393, from 458 nm to 456 nm) as the phosphor particle size of SMS-SOC decreases compared with the phosphor result of SMS-SO. This may be because of the quantum size effect (QSE) of the nanometer phosphor increases the kinetic energy of the electrons and results in a larger band gap, and thus need higher energy to excite the luminescent powders [16]. The luminescence is viewed as the typical emission of Eu^{2+} ascribed to the 4f-5d transitions. Interestingly, there are additional narrow bands overlapping for SMS-SO sample in long wavelength side of the Eu^{2+} emission band. In general, it can be said that there are two basic factors [17] that influence the emission radiation of a phosphor. The first one is the strength of the crystal field at the sites of the luminescing ions and the second is the degree of covalence of these ions with the surrounding oxygen ions. However, a detailed reaction is still not known and the additional emission shown by SMS-SO sample needs to be further studied.

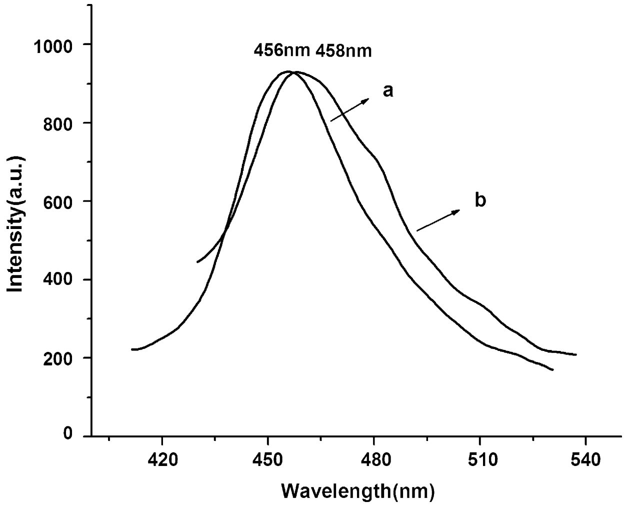

Fig. 4. Emission spectra of $Sr_2MgSi_2O_7$:Eu,Dy prepared by (a) $Si(OC_2H_5)_4$ and (b) SiO_2 source (monitored wavelength: (a) $\lambda_{ex} = 335$ nm; (b) $\lambda_{ex} = 350$ nm).

The decay characteristics of SMS-SOC and SMS-SO phosphors passed through a 100 mesh sieve and weighed 0.015 g under excitated by 9 W tricolor luminescent lamp for 15 min at room temperature is shown in Fig. 5 (the afterglow

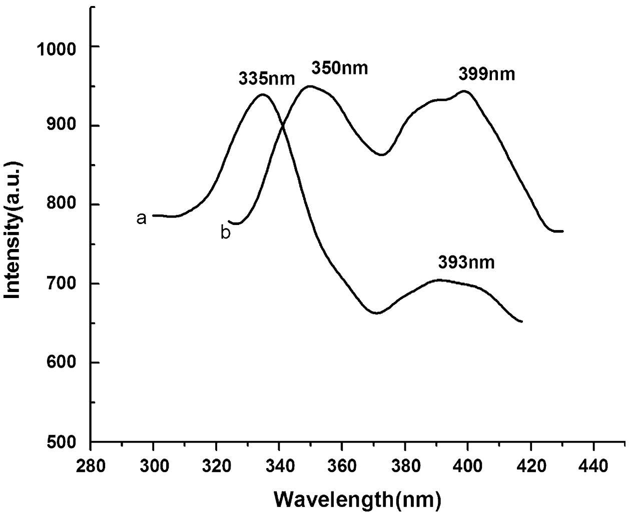

Fig. 3. Excitation spectra of $Sr_2MgSi_2O_7$:Eu,Dy prepared by (a) $Si(OC_2H_5)_4$ and (b) SiO_2 source (monitored wavelength: (a) $\lambda_{em} = 456$nm; (b) $\lambda_{em} =$ 456 nm).

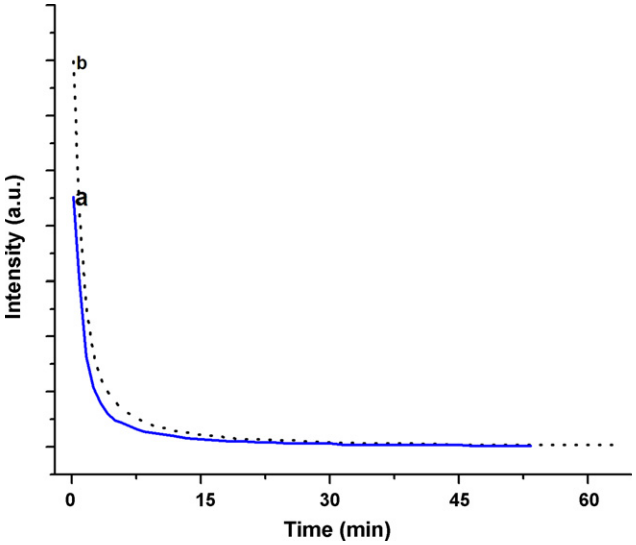

Fig. 5. Decay curve of $Sr_2MgSi_2O_7$:Eu,Dy prepared by using (a) $Si(OC_2H_5)_4$ and (b) SiO_2 as the starting materials.

persistent time from the initial intensity to 1 mcd m^{-2} are determined). The initial intensity of nanometer SMS-SOC is lower than that of the SMS-SO (also refer Fig. 5a and b), and that the SMS-SOC phosphor decays more rapidly than SMS-SO. The reason may be that the nanometer particles make the phosphor crystallize easily and completely during combustion, which may lead to the amount of defects in the inner phosphor decrease and fewer crystallographic distortions as well as shallower trap level than that of phosphor obtained from SiO_2 source, so that the intensity of afterglow lowers and the decay of afterglow is faster. In addition, many defects are dispersed on the surface of phosphor because of the large surface area of SMS-SOC, and which possibly result in relative less amount of luminescent center Eu^{2+} in $Sr_2MgSi_2O_7$ lattice. Of course, the material reason need to be further investigated, and relative research is under processing.

4. Conclusion

The $Sr_2MgSi_2O_7$:Eu,Dy nanophosphor powders can be synthesized by combustion processing with ultrasonic dispersing technique. $Si(OC_2H_5)_4$ and SiO_2 are employed as the starting materials of silicate host, respectively. Analytical result shows the phosphor prepared by employing $Si(OC_2H_5)_4$ has purer $Sr_2MgSi_2O_7$ phase with smaller particles size of about 20 nm. Compared with the phosphor obtained from SiO_2, the blue shift of main peaks of excitation and emission of nanometer phosphor occurs. This will probably provide its potential applications in FED, etc. Combustion method lowers the cost and can save energy, and can be operated easily.

Acknowledgements

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