

Preparation of the ultrafine $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ needle-like phosphor and its optical properties

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Abstract

$\text{Sr}(\text{NO}_3)_2$, NH_4HCO_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$ and $\text{Dy}(\text{NO}_3)_3$ are used as the raw materials for the preparation of $\text{SrCO}_3\text{-Al}_2\text{O}_3\text{-RE}(\text{OH})_3$ (RE: Eu, Dy) precursor by the ‘soft’ chemical synthesis method, which is convenient to make the components uniformly. The ultrafine needle-like phosphors with high brightness and long afterglow were obtained by sintering the precursor at high temperature and at weak reductive atmosphere (1.5% H_2 and 98.5% N_2) for the first time. The average particle size of the $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ needle-like phosphors was less than 100 nm as observed by the transmission electron microscopy (TEM) and its optical properties have been studied systematically. The results indicated that the main peaks in the emission spectrum and the excitation spectrum shifted to the short wavelength compared with the phosphor prepared by the traditional ‘ramic’ method. The decay speed of the afterglow prepared by this method was faster than that of the ceramic method. As for the mechanism of long afterglow of the $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ phosphor, Dy^{3+} played an important role and acted as the trap levels in the system, which lied in between the excited state and the ground state of Eu^{2+} . It is the holes thermally released from the trap levels that resulted in the long afterglow phenomenon of phosphors. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Precursor; Long afterglow; Phosphor; Emission spectrum; Trap level; Optical properties

1. Introduction

The long afterglow photoluminescence materials have the particular properties — storing light energy and glowing slowly at dark place. That is to say, the materials can absorb the visible lights, store the energy, and then release the energy as the visible lights [1]. Compared with sulfide phosphorescent phosphors, $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ phosphor is chemically stable and shows excellent photo-resistance, which has excellent properties such as high brightness, no radiation, safety, long duration, and environmental capability [2–4], which resulted in its wide applications in many fields. It may be used as luminous paints in different places, such as highway, railway, airport, ferry, and on the facade of buildings. In addition, luminous powders can be added to the transparent glaze to form luminous glaze used on the surface of different ceramics products. It can also be used in textile field, the dial plates of night-watch, automobile, ship and other instruments [5].

In the present work, SrAl_2O_4 is employed as the matrix materials, and doped with rare earth elements (e.g. Eu, Dy) as the activator and co-activator. The

$\text{SrCO}_3\text{-Al}_2\text{O}_3\text{-RE}(\text{OH})_3$ (RE: Eu, Dy) precursor powders were prepared by the soft chemical synthesis method, and the ultrafine needle-like photoluminescent phosphors with high brightness and long afterglow were obtained by sintering the precursor at high temperature and at weak reductive atmosphere.

2. Experimental procedure

Samples with the $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ general composition were synthesized at 1100 and 1200°C by the soft chemical method combined with the solid-state reaction technique under a weak reductive atmosphere of 1.5% H_2 and 98.5% N_2 . All starting materials were of the analytical purity.

The morphology and particle size of the prepared phosphors powders were observed by transmission electron microscopy (TEM). Crystal structures of samples were checked by means of a Rigaku Denki diffractometer using $\text{Cu K}\alpha$. The room temperature luminescence measurements of powders were carried out with a fluorescence spectrophotometer using a Xenon arc lamp as excitation source. The decay curve of afterglow was measured by the brightness meter connected with the data collection system.

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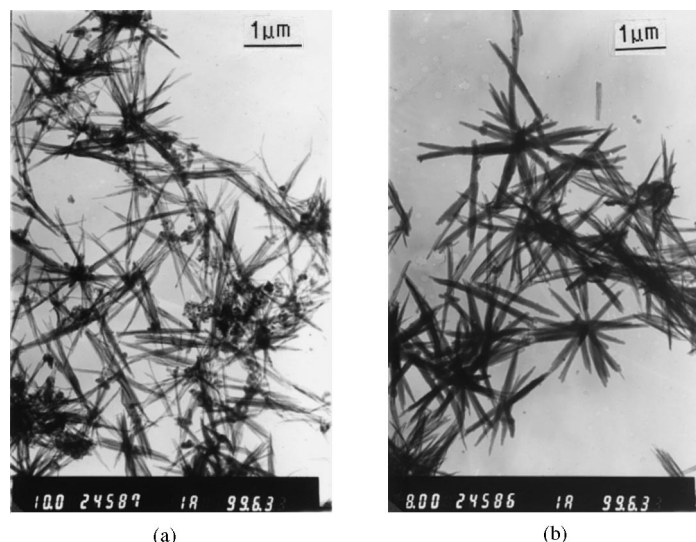


Fig. 1. The TEM of $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ phosphor powders sintered at different temperature. (a) Sintered at 1100°C ; (b) sintered at 1200°C .

3. Results and discussion

Fig. 1 shows the phosphor powders morphology and the crystal particle size sintered at the temperature of 1100 and 1200°C for 2 h separately by TEM. The graphs illustrate that the powders particle are homogeneous needle-like, and the phosphors prepared at 1100°C contained some small particles. With the increase in sintering temperature, the average diameter of SrAl_2O_4 needle-like crystal is increased, but both of them are less than 100 nm . Compared with the phosphors prepared by the traditional ceramic method, the sintered temperature decreased by about 150°C due to the high activity of nanometer Al_2O_3 and the homogeneous components, and the needle-like crystals are apparently different from the traditional elliptic or circular SrAl_2O_4 crystal particles [6].

SrAl_2O_4 has two phases, a high-temperature hexagonal phase (β -phase) and a low-temperature monoclinic phase (α -phase). The transition temperature occurs at 650°C [7]. Fig. 2 indicates the phase composition of the needle-like

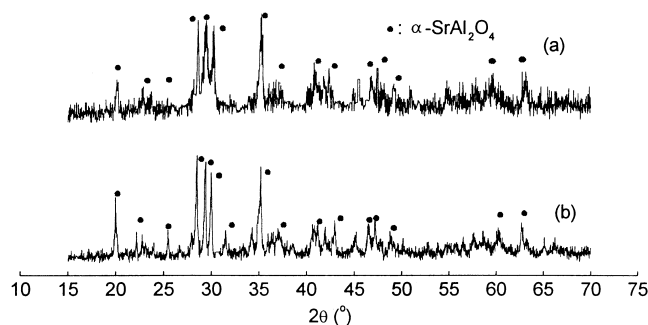


Fig. 2. The X-ray diffraction spectrum of phosphors sintered at different temperature. (a) 1100°C ; (b) 1200°C .

phosphors, the results proved that the phosphors prepared in this work are all α -phase, and the little amount of doped rare earth ions (about $0.005\sim 0.01\text{ at.}\%$) have almost no effect on the SrAl_2O_4 phase composition. The growth mechanism of the needle-like crystal is unknown, but these needle-like phosphors are very useful to apply in the constructed materials to detect the damage of bridge or the high buildings, and may also be used as the decorative materials for the hotel, the plaza, etc., the relative research works are processing.

The excitation and emission spectra at room temperature of $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ prepared by the different methods are shown in Figs. 3 and 4. The results indicate that the main peaks intend to shift to shorter wavelength. It is observed that the optical absorption edge shifts to the blue (from 260 to 255 nm , and 320 to 316 nm) as the phosphor particle size decreases. We think this may be associated with the quantum size effect of the nanometer phosphor, which increased the kinetic energy of the electrons and resulted in a larger band gap, and thus required higher energy to excite the luminescent powders. Simultaneously, the emission maximum shifted to shorter wavelength (from 520 to 508 nm), we think this may be caused by the prepared technology, which resulted in some changes of the crystal field around Eu^{2+} . Although the $4f$ electrons of Eu^{2+} are not sensitive to lattice environment due to the shielding function of the electrons in the inner shell, the $5d$ electron may couple strongly to the lattice. Consequently, the mixed states of $4f$ and $5d$ will be split by the crystal field, which may lead to the blue shift of its emission peak.

Fig. 5 shows the decay curve of $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ phosphor powders. The results indicate that the initial intensity of phosphor powders prepared by the soft chemical synthesis is almost same as the phosphor powders prepared by the ceramic method after exciting for 3 min. But after the removal of the excitation source, their afterglow intensity are very

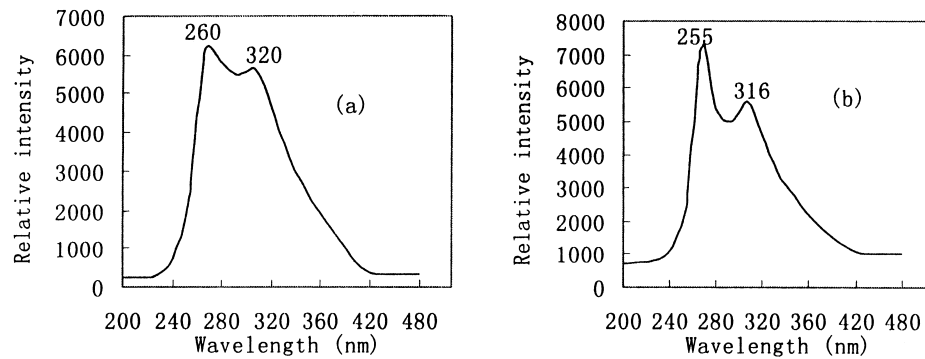


Fig. 3. Excitation spectra of SrAl₂O₄:Eu,Dy prepared by the different precursor. (a) Phosphor prepared by the ceramic method; (b) phosphor prepared by the soft chemical synthesis.

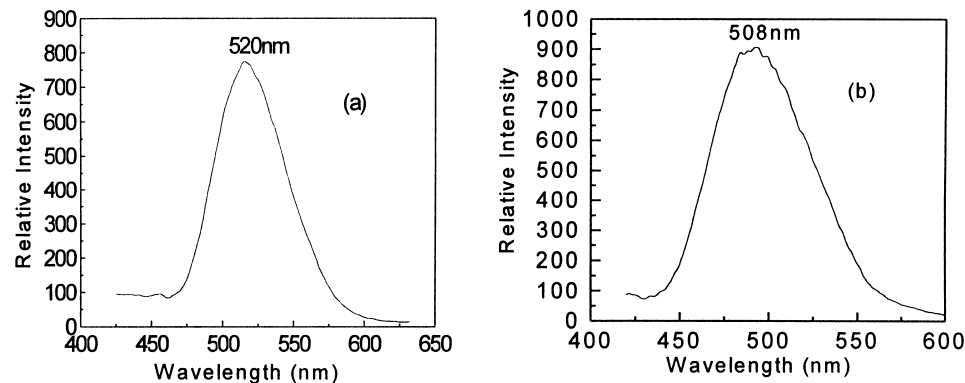


Fig. 4. Emission spectra of SrAl₂O₄:Eu,Dy prepared by the different precursor. (a) Phosphor prepared by the ceramic method; (b) phosphor prepared by the soft chemical synthesis.

much different, and the phosphor prepared by this method decayed more rapidly than one prepared by the ceramic method. The reason may be that the phosphor particles are so small that Eu and Dy ions can be transferred rapidly into

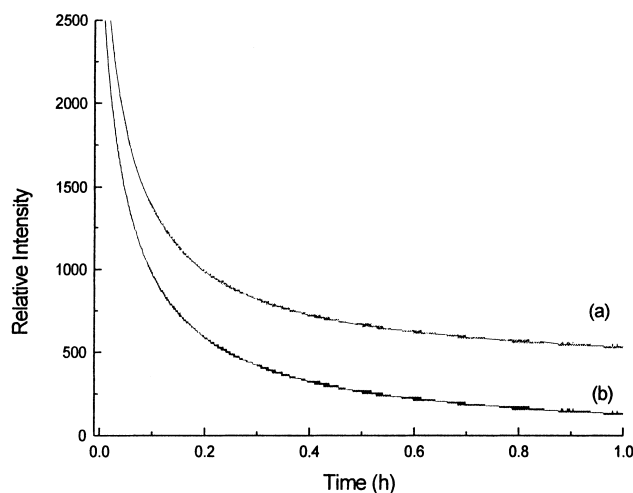


Fig. 5. The decay curve of SrAl₂O₄:Eu,Dy phosphor powders after exciting for 3 min. (a) Phosphor prepared by the ceramic method; (b) phosphor prepared by the soft chemical synthesis.

the SrAl₂O₄ crystal lattice during heat-treatment process. In addition, a lot of defects are dispersed on the surface of phosphors because of the high surface area of the nanometer powders, and it is convenient to form more luminescent centers on the surface. On the other side, smaller particles made the phosphor crystallize easily and completely, which resulted the amount of defects decreased in the inner phosphor, so that the relative intensity of afterglow lowered. In addition, we found that the decay process also contained the rapid-decaying process and the slow-decaying process. The decay curve of the afterglow is nonexponential, and cannot be explained simply by thermally activated detrapping processes. As for the mechanism of the long afterglow, it is the hole trapped-transported-detrapped process that resulted in the properties of long afterglow of SrAl₂O₄:Eu²⁺,Dy³⁺ phosphor. Among these, the Dy³⁺ played an important role and worked as traps of holes (trap levels), the trap levels lied in between the excited state and the ground state of Eu²⁺. After excited by the ultraviolet lights, electron and hole pairs were produced, and some free holes transported in the conduction band were captured by the Dy³⁺ traps. When the excitation source was cut off, some holes captured by the Dy³⁺ traps were thermally released slowly and relaxed to the excited state of Eu²⁺, finally, returned to the ground state of Eu²⁺ accompanied with emitting the lights. This is the

reason why phosphor maintained a long afterglow period at a relatively low luminescent intensity level ($\geq 0.32 \text{ mcd m}^{-2}$).

4. Conclusion

Based on the above research, the $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ needle-like phosphor can be synthesized by sintering the ultrafine precursor $\text{SrCO}_3\text{-Al}_2\text{O}_3\text{-RE(OH)}_3$ (RE: Eu, Dy) powders by this technology. Analytical results showed that the needle-like phosphor powders have formed $\alpha\text{-SrAl}_2\text{O}_4$ phase at 1100°C , and the average particles size is less than 100 nm. When compared with the traditional ceramic method, with the decreasing the crystal size of phosphor, the blue shift of main peaks of excitation and emission of the phosphors occur. After removal of excited source, the $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ phosphor can maintain a long afterglow period at a relative intensity level.

Acknowledgements

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