

Synthesis of high-brightness fine SrAl₂O₄: Eu, Dy phosphor by gel-casting and solid-state reaction process

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High-brightness fine SrAl₂O₄: Eu²⁺, Dy³⁺ phosphors were prepared by gel-casting and solid-state reaction process using 1:1 ratio of Al₂O₃ and SrCO₃ as the starting materials. Scanning electronic microscope (SEM) morphology shows that the specimens presintered or sintered by different temperatures have uniform grain size and pores. The resultant powders ground by ball-milling for 24 h were around 1 μm from transmission electronic microscope (TEM) photograph. The wide range of excitation spectrum of the phosphors indicates that the luminescent materials can be excited by light from ultraviolet ray to visible light and the maximum emission wavelength of the phosphors is found mainly at λ_{em} of 520 nm, the corresponding colors of emission light are green. The afterglow decay tendency of phosphors can be summarized as three processes: initial rapid decay, intermediate transitional decay and very long slow decay. Afterglow decay curves coincide with formula I=At⁻ⁿ.

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1. Introduction

Inorganic phosphors have been extensively investigated for the application to various types of optical and electrical fields, such as lighting in weak light environment, indicating, energy transfer, and light-storing. Traditionally, SrAl₂O₄: Eu²⁺, Dy³⁺ phosphors are prepared at high temperatures for a long time via solid-state reaction process, due to insufficient mixing and the low reactivity of raw materials, several impurity phases such as Al₂O₃ and SrO easily exist in the products. Moreover, the products fabricated by solid-state reaction process are too solid to grind. For overcoming the drawbacks of the solid-state reaction process, several wet chemical methods such as co-precipitation, combustion, and spray pyrolysis have been developed to fabricate the SrAl₂O₄: Eu²⁺, Dy³⁺ phosphors [1~4]. Although SrAl₂O₄: Eu²⁺, Dy³⁺ can be obtained at low temperatures via these methods, it is difficult to commercial produce.

Recently, it was reported that gel-casting process was explored to fabricate porous ceramics [5, 6]. This is because the successfully gel-cast part consists of a well distributed three component system comprising the ceramic particles, gel matrix, and the polymer strands that cross-link throughout the entire inter-particle spaces. In the present work, we synthesized SrAl₂O₄: Eu²⁺, Dy³⁺ phosphors by a unique combination of the gel-casting and solid-state reaction process. By this process, we prepared single-phase SrAl₂O₄: Eu²⁺, Dy³⁺ phosphor sinters with uniform distribution pores. The particle size of the phosphor can be easily obtained at several micrometers by ball milling and sieving. Because of so little shrinkage, all samples in this experiment possess low strength and are

fragile.

2. Experimental

Phosphors were prepared by the gel-casting and solid-state reaction method. The starting materials used in the preparation of these phosphors were SrCO₃, Al₂O₃, Eu₂O₃, Dy₂O₃ and H₃BO₃ powders of purity greater than 99.9%. The chemicals, mixed in aqueous monomer [acrylamide, C₂H₃CONH₂ (AM) and N,N'-methylenebis-acrylamide, (C₂H₃CONH)₂CH₂ (MBAM), AM:MBAM 20:1 (by weight)] solution with a concentration of 10wt% in stoichiometric amounts of the starting materials, were thoroughly mixed by a ball-milling for 24 h. The resulting slurry, with the initiator ammonium bisulphate (NH₄)₂S₂O₈ (1.6 wt% of organic monomers) and a little catalyst N,N,N',N'-tetramethylethylenediamine (TEMED), was cast into a mold and solidified at 80 °C for 30 min. The dried gel-cast were fast dried in an oven at 100 °C and calcined in an oxide atmosphere at 1350 °C for reducing the carbon concentration, followed by a firing in a reducing atmosphere (90N₂+10%H₂) at 1500 °C. The calcined samples cooled with the furnace, and were ground into powders by ball-mill for 24 h.

Microstructure characterization of all specimens was carried out on a Philip XL30ESEM scanning electronic microscope (SEM). The particle size and morphology of powders were examined using the transmission electronic microscope (TEM; Hitachi JEOL-100CX-II). The photoluminescence (PL) properties of the powders were measured using a Hitachi F-4500 fluorescence spectrophotometer at room temperature. A 150W Xe lamp

was used as a multi-wavelength light source.

The porosity of the porous samples after sintering was determined primarily by the green density and shrinkage, as well as weight change during the sintering. These parameters could explain why the porous samples had high porosity. Firstly, the green bodies were prepared by gel casting with relatively low solid contents, and the green densities were rather low. Secondly, the high adhesive glass phase restricted the shrinkage during the sintering.

3. Results and discussion

The microstructures of specimen presintered at 1350 °C for 1h are given in Fig. 1. It can be seen that pores in specimen are the open-pore state. This is beneficial in maintaining good connection between the matrixes at the center of specimens and reducing atmosphere. SEM photograph of calcined at 1500 °C in a reducing atmosphere (90N₂+10%H₂) is shown in Fig. 2. From Fig. 2, it can be seen that there is homogeneous micrometer-sized grains and pores in the sample, which is ideal for consequent grinding process.

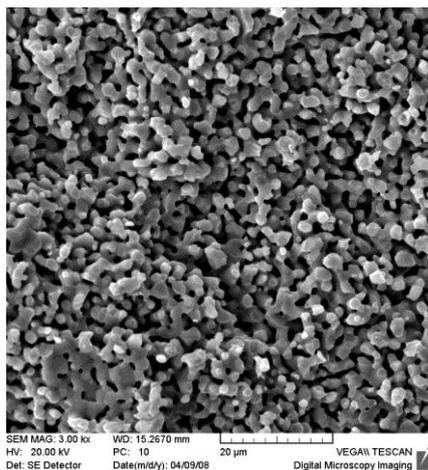


Fig. 1. Scanning electron micrograph of specimen presintered at 1350 °C for 1 h in an oxide atmosphere.

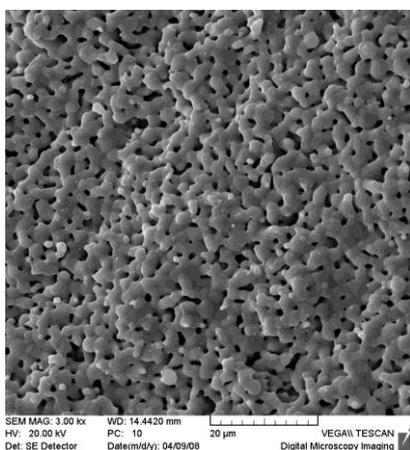


Fig. 2. Scanning electron micrograph of specimen sintered at 1500 °C for 3 h in a reducing atmosphere.

Fig. 3 shows a TEM image of the ground powders ball-milled for 24h. The size distribution was calculated based on a log-normal function and image analysis program. Average diameter around 1 μm was observed.

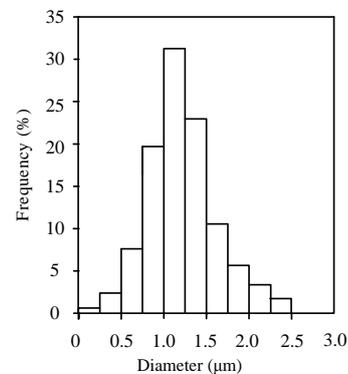
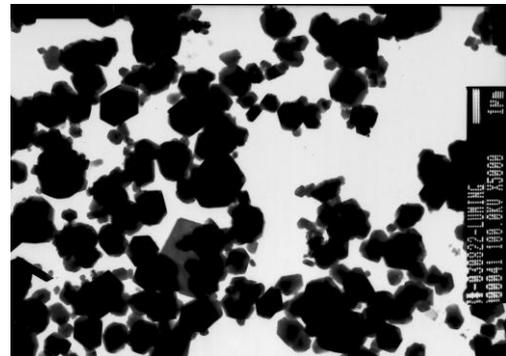


Fig. 3. TEM images (left) and the corresponding particle size histograms (right) of the powders ground by ball-mill for 24 h.

Fig. 4 shows the excitation and emission spectrum of the SrAl₂O₄: Eu, Dy powder. The phosphor is excited efficiently by light from ultraviolet ray to visible light and have a broad-band continuous excitation spectrum. The maximum excitation wavelength of phosphors is found mainly at of peak 360 nm. The emission spectrum of phosphors is also a broad-band continuous spectrum and the maximum emission wavelength of phosphors is found mainly at of peak 520 nm, the corresponding color of emission light is green.

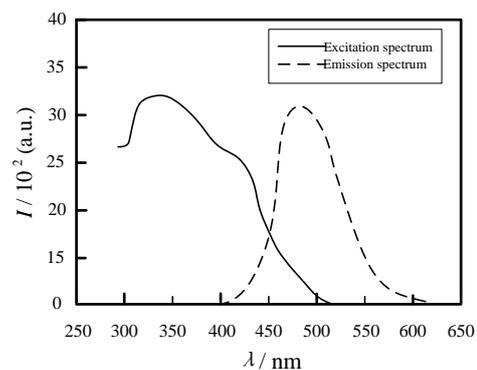


Fig. 4. Excitation and emission spectrum of SrAl₂O₄: Eu, Dy powder.

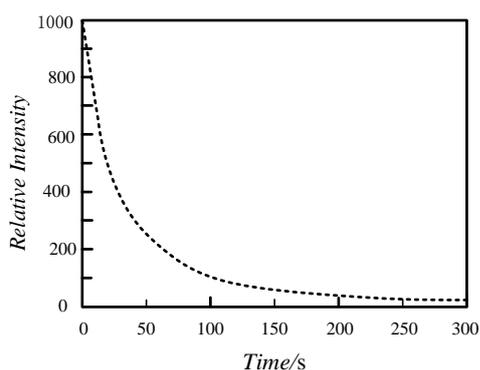


Fig. 5. Decay curve of SrAl₂O₄: Eu, Dy powder.

The afterglow decay curve of the phosphor is shown in Fig. 5, the excitation time is 20 min, and 365 nm xenon lamp is used as light source. Fig. 5 indicates that the afterglow decay tendency of the phosphor can be summarized as three processes: initial rapid decay, intermediate transitional decay and followed by a very long slow decay. By the analysis of OriginPro software, the afterglow decay curves coincide with formula $I=At^{-n}$. The values of A and n are respectively 3622.46 and 0.8194. The initial rapid decay is due to short survival time of electron in Eu²⁺, the intermediate transitional decay is due to the capture of Eu²⁺ by shallow trap energy center and the very long slow decay is due to very deep trap energy center of Dy³⁺ [7]. According to theory, afterglow phenomena can be produced only when appropriate trap energy level is existed. If the trap energy level is shallow, electrons in the trap can be excited easily and come back to the excited state, it results in short afterglow time. If the trap energy level is quite deep, higher energy is needed when excited electrons in trap come back to the excited state, so electrons are only stored in trap energy and afterglow phenomenon is not observed. When Dy³⁺ replaces the alkali earth metals Sr of SrAl₂O₄ (the replacement is not equivalent), the depth of trap has relationship to the composition and structure of host. SrAl₂O₄: Eu, Dy phosphor is with monoclinic crystal structure, so appropriate trap can be produced and afterglow phenomena can be observed.

4. Conclusions

Long afterglow phosphors SrAl₂O₄: Eu, Dy whose average size was around 1 μm was synthesized successfully by gel-casting and solid stated reaction method. The phosphor is excited efficiently by light from ultraviolet ray to visible light, the excitation spectrum and the emission spectrums of the powder are broad-band continuous spectrums. The afterglow decay tendency of the phosphor can be summarized as three processes: initial rapid decay, intermediate transitional decay and followed by a very long slow decay. Afterglow decay curves coincide with formula, $I=At^{-n}$.

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