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Synthesis and properties of green phosphor $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ for field emission displays by an environmentally clean technique

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Abstract

An environmentally clean synthesis technique is reported for preparing the green phosphor $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$. This method is based on solid state chemical reactions with the use of raw materials: sodium dimethyldithiocarbamate, tetramethylammonium chloride, gallium nitrate, europium nitrate, strontium sulfide and sulfur. The method is shown to produce powders with quasi-spherical shape, smooth surface morphologies, uniform particle size distribution and high luminous efficiencies (~ 20.5 lm/W at 2 kV and 30.8 lm/W at 5 kV). © 2000 Elsevier Science Ltd. All rights reserved.

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Field emission displays (FEDs) are an important flat panel display technology that offer the potential of achieving comparable or superior levels of performance as the cathode ray tubes (CRTs), but in a flat panel package. Because FEDs operate at much higher current densities and lower excitation voltages than CRTs, the requirements for FED phosphors are different than for CRT phosphors. These requirements include high efficiency at low excitation voltage (≤ 5 kV), high resistance to current saturation, high chemical and thermal stability, long service life-time at high current densities and equal or better chromaticity than CRT phosphors. In developing FEDs, the green phosphor is essential since it must provide more than 60% of the light output [1–3]. Thus the development of phosphor materials is one of the key steps for flat panel FEDs. In previous work we have shown that the europium doped strontium thiogallate ($\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$) is an attractive green phosphor candidate due to its high brightness at low excitation voltage and good saturation properties [4,5].

Conventionally, $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ is synthesized by a flux method, in which a mixture of alkaline earth metal carbonate, gallium oxide, rare earth metal oxide and flux agents is fired at high temperatures under flowing hydrogen sulfide

(H_2S) or carbon disulfide (CS_2) [6–10]. Since H_2S is a very toxic gas and can cause serious pollution, the exhausted gas must be handled very carefully. Kobayashi et al. [11] reported an alternative technique to prepare calcium and europium thiogallates. In their method H_2S was replaced by inert Ar gas, but no further optical properties and optimized experimental conditions were reported. In our study, this environmentally clean technique was employed for the synthesis of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ powder. The advantage of this technique is that the toxic H_2S gas is replaced by Ar gas, eliminating environmental hazard. The microstructure and the properties of the synthesized phosphor powders are characterized.

In this technique, strontium sulfide (SrS , 99.99%), gallium nitrate ($\text{Ga}(\text{NO}_3)_3$, 99.99%), europium oxide (Eu_2O_3 , 99.99%), nitric acid (HNO_3), sodium dimethyldithiocarbamate (DMDTCA, $(\text{CH}_3)_2\text{NCS}_2\text{Na}$, > 98%) and tetramethylammonium chloride (TMAC, $(\text{CH}_3)_4\text{NCl}$, 97%) were used as raw materials. First, europium nitrate was obtained by dissolving Eu_2O_3 in hot HNO_3 . Secondly, gallium nitrate was reacted with DMDTCA to form the gallium complex, and europium nitrate was reacted with DMDTCA and TMAC to form the europium complex. The gallium complex and europium complex were then mixed with SrS and S and to achieve a good stoichiometry

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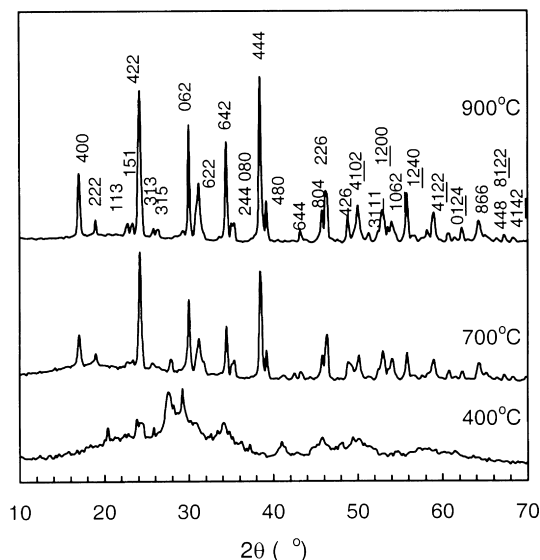


Fig. 1. X-ray diffraction patterns of phosphor particles fired at different temperatures, showing that the crystallization is completed at about 900°C and the powder is single phase.

in the firing phase. This mixture was ball-milled in absolute ethanol for 20 h. It is clear that oxygen was completely eliminated from the raw materials. The dried mixture was then fired up to 1000°C for 5 h to form crystalline thiogallate phosphor powders. Finally, a second ball-mill process was introduced to break agglomerations present in the powders, after which the powders were re-heated at lower temperatures to improve crystal quality. A self-defining optimization method was used to optimize various experimental parameters. In this study the concentration of the Eu dopant was controlled to be 4 mol.%.

The phases formed at different temperatures were identified by powder X-ray diffraction (Rigaku, D-MAX-B) and the powder morphologies were studied by scanning electron microscopy (SEM, Hitachi S-4100). The particle size distribution was measured by a Microtrac-X100 particle size analyzer. The PL measurement was conducted using a CO₂ laser with a wavelength of 275 nm and at power of 15 mW. The brightness was normalized in reference to that for a standard sample used in the entire experiments. The CL was measured using deep powder patches in an ultra-high-vacuum chamber as reported previously [12].

Fig. 1 shows the X-ray diffraction patterns of the powders

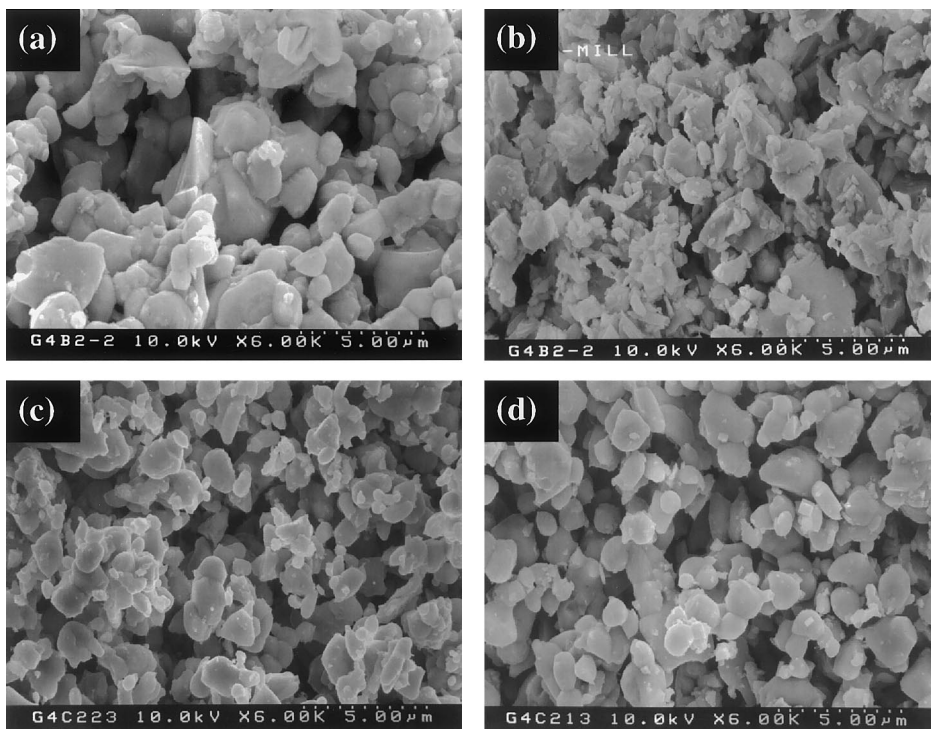


Fig. 2. (a) Morphology of the as-fired particles, exhibiting agglomerations between particles; (b) morphology of particles after ball-mill, showing damaged particles and irregular shape; (c) morphology of particles annealed at 800°C for 5 h; and (d) annealed at 850°C for 5 h, showing improved particle shape and surface smoothness.

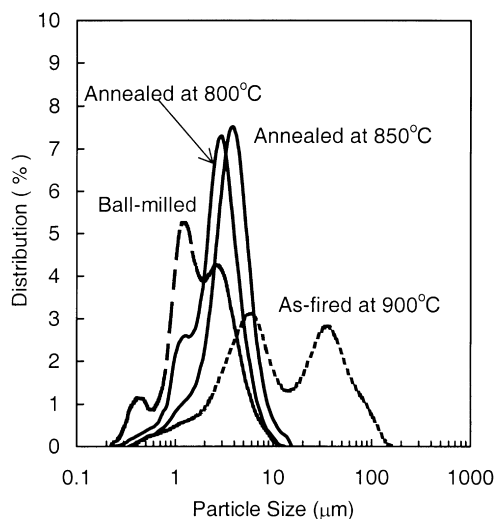


Fig. 3. Particle size distribution before and after heat treatment, showing that after heat treatment the particle size distribution is much more uniform than that of the as-fired particles and ball-milled.

fired at different temperatures. SrGa_2S_4 has an orthorhombic structure with $a = 2.0840$, $b = 2.0495$ and $c = 1.2212$ nm. The as-prepared compound was amorphous and started to decompose into sulfides after being fired at $\sim 400^\circ\text{C}$. A small fraction was crystallized at this temperature. Further heating the compound to $\sim 700^\circ\text{C}$ led to the formation of crystalline strontium thiogallates, and the complete crystallization was finished at $\sim 900^\circ\text{C}$.

The morphologies of the thiogallate powders, which were processed at different conditions, are shown in Fig. 2. It is apparent that the as-fired powders have large particle sizes and there are many agglomerations observed among particles (Fig. 2(a)). Agglomerations can cause low layer packing densities, leading to strong light scattering and a subsequent decrease in the screen efficiency. In order to break up the agglomerations and improve the quality of the powders, the as-prepared thiogallate powders were ball-milled using ceramic balls for 4 h in absolute ethanol and then re-crystallized by heat treatment at 800°C and 850°C for 5 h. After ball-mill, the particles were damaged and became irregular (Fig. 2(b)). After heat treatment, the particles became quasi-spherical and their surface smoothness was improved, especially at 850°C (Fig. 2(c) and (d)). Both the particle size and surface smoothness are critically important for improving the low voltage luminous efficiency. Also, the latter is essential for subsequently coating the sulfide phosphor with oxides to reduce the contamination of the FED electrodes and improve its aging performance.

Fig. 3 presents the particle size distribution of the powders before and after the final heat treatment. The particle size distribution of the as-fired powder was wide and

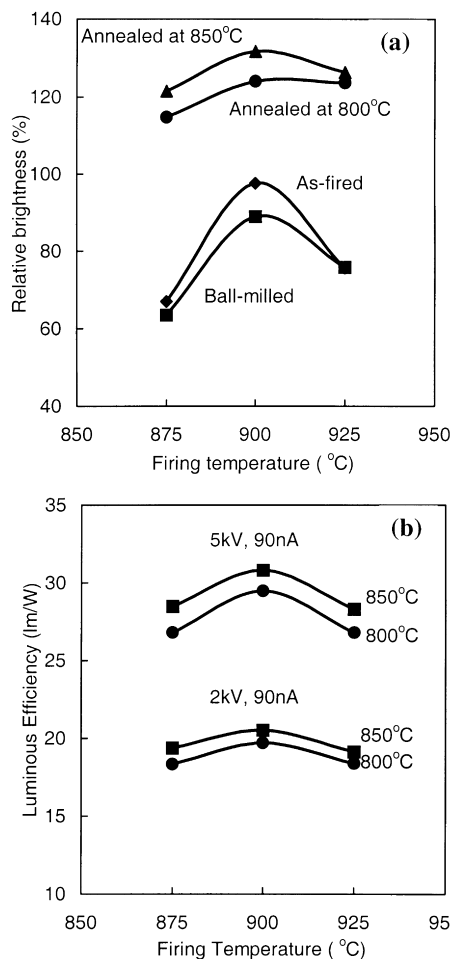


Fig. 4. Comparison of luminescent properties of the powders before and after anneal, showing the improved efficiency.

bimodal and indicates an average particle size of $\sim 22.0 \pm 10.0 \mu\text{m}$. After ball-milling the average particle size decreased to $\sim 2.2 \pm 1.3 \mu\text{m}$, but the distribution became tri-modal. A further heat treatment at 800°C for 5 h resulted in a slightly bimodal distribution with an average particle size of $\sim 3.0 \pm 1.2 \mu\text{m}$. Replacing this treatment by an anneal at 850°C gave a more uniform particle size with a average particle size of $\sim 4.0 \pm 1.0 \mu\text{m}$. The morphology and particle size distribution are better than conventional technique.

Both the photoluminescence intensity (PL) and cathodoluminescent (CL) efficiency were measured with respect to the final firing temperature and different subsequent heat treatments (Fig. 4). From Fig. 4 it can be found that firing at 900°C for 5 h gives the highest brightness. Ball-mill slightly decreased the PL brightness. However, both the PL and CL were improved dramatically after heat treatment. For the sample fired at 900°C for 5 h, the brightness was improved by $\sim 35\%$ after annealed at 850°C for 5 h. The luminous efficiency at higher excitation voltage is due to

the increase in the interaction volume between the incident electrons and the phosphor particles. That the higher luminous efficiency after ball-mill and anneal than that of the as-fired powders correlates with the observation that after ball-mill and anneal, the surface morphology is smoother, the particle size is smaller and the particle size distribution is more uniform. All of these properties will enhance screen efficiency and aging properties by enabling a more dense powder layer with less light scattering [12]. Further processing improves the powder quality.

The emission peak of this phosphor was located at ~ 536 nm, and the Commission International de l'Eclairage (CIE) chromaticity coordinates were $x = 0.27$ and $y = 0.68$. This is significantly better than that of the commercial green phosphor ZnS:Cu, whose emission peak and CIE coordinates are 520 nm and $x = 0.28$ and $y = 0.53$, respectively [13].

In this paper we have presented an environmentally clean technique and optimized the processing parameters for the synthesis of the green phosphor $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$, which has great potential for FED applications. In this method, H_2S or C_2S is replaced by Ar gas. This reduces the difficulty in handling the exhausted gases and potentially provides an environmentally cleaner synthesis method for sulfide phosphors. The powders prepared by this method also have a very uniform particle size distribution, smooth surfaces and a quasi-spherical shape, which are necessary for enhancing the low voltage properties by coating with oxides. Also this method can be used to prepare the blue phosphor strontium thiogallate doped with cerium ($\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$) and other sulfides and scaled up for large quantity industrial production.

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