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Synthesis of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ Nanometer Phosphors by Detonation and Combustion Method*

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Abstract: The $SrAl_2O_4:Eu^{2+},Dy^{3+}$ (SED) nanometer phosphors were synthesized at lower temperature by detonation and combustion method, respectively. The effects of synthesis conditions, annealing temperature on the growth behavior, the particle morphologies and optical properties of the as-prepared SED particles were contrasted. It was showed that the mean size of the SED particles prepared by detonation method increased gradually with increasing heat treatment, and that the mean size of the SED particles prepared by combustion method decreased firstly and then increased quickly and had a minimal value at 600 ℃. The mean size of the SED particles prepared by detonation method increased more quickly than that of the SED particles prepared by combustion method at same annealing temperature. Finally, the mechanism for the long afterglow was discussed and some suggestions on how to improve the synthesis methods were also presented.

Key words: detonation method; combustion method; nanometer phosphor powders; optical properties

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1 Introduction

As a kind of photon energy-storing materials, persistent phosphors can absorb the visible lights and store the energy. After the excitation source is turned off, the stored photon energy can be gradually released as visible light, which leads to long persistent luminescence in the darkness[1-2]. The long phosphorescent phosphors not only can be used as traditional phosphor materials, but can be used as optoelectronic materials and photovoltaic electronic equipments, such as amplifier, optical fibers, optical storage and displaying equipments. Even it may be a promising material applied in the fields of information process, new energy, life sciences, etc. In recent years, strontium aluminate phosphors doped with rare earth ions, such as $SrAl_2O_4:Eu^{2+},Dy^{3+}$ (SED)[1]; $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$[3]; $SrAl_4O_7$[4], $SrAl_{12}O_{19}$[5], have attracted much attention. In contrast to traditional long phosphorescent phosphors such as ZnS:Cu phosphor, strontium aluminate phosphors have many excellent properties, such as high quantum efficiency[6], long persistence and better stability[7-8].

Much attention has been focused on preparing the long phosphorescent phosphor. A variety of methods, such as solid-state reaction synthesis method[9], sol-gel method[10], hydrothermal method[11], combustion method[12], co-precipitation method[13], floating zone technique[14], have been summarized

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in Ref. [15]. All those methods were conducted in liquid phases so that each component can be accurately controlled and uniformly mixed. Those methods have some drawbacks more or less, however. For example, solid-state synthesis method requires rigorous synthesis conditions such as high temperatures, weak-reducing atmosphere, and expensive equipment and high consumption of energy are also needed. Meanwhile the matrix composition, structure and luminescent properties of the phosphors can be affected by the synthesis conditions. In order to obtain ultrafine phosphor particles, the as-prepared phosphor powders must be grinded. The process easily introduces additional defects and greatly reduces the luminescence efficiency. While the process routines of the sol-gel and the co-precipitation method to prepare the precursor powders are complicated and the duration is long[16]. Detonation method is an efficient technique for preparation of nanometer powders because of the good mixing of the starting materials. The preparation of the SED nanometer phosphors by detonation method has been presented in Ref. [17]. While combustion method is also a promising method to some extent to prepare the nanosized aluminate phosphors[16]. In order to further explore a synthesis method fit for the preparation of SED nanometer phosphor powders in quantity, it is necessary to find the similarities and differences of the two methods.

In this study, the preparation of the SED nanometer phosphors by detonation and combustion method at lower temperatures was presented. The effects of synthesis conditions, particle morphologies, thermal treatment and optical properties of SED prepared via detonation or combustion method were formulated, respectively. The mechanism for the long afterglow was discussed and some suggestions on how to improve the synthesis methods were also presented.

2 Experimental

2.1 Phosphor Particles Preparation

$Al(NO_3)_3 \cdot 9H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, $CO(NH_2)_2$, $SrNO_3$ and $Dy(NO_3)_3 \cdot 6H_2O$ were employed as the raw materials, and some quantities of boric acid (H_3BO_3) were also added as a flux[18]. They were weighed at a certain molar ratio. Then the highly transparent primrose sol was obtained after the mixtures were liquated in a beaker at 120 ℃ for over a dozen of hours. Then the sol was divided into two parts. One part was covered with RDX outside in the proportion of 1∶1, and then detonated by a detonator in an explosion vessel and detonation soot was obtained. The preparation process was described detailedly in Ref. [17] just as shown in Fig. 1. The other part of the sol was combusted for 5 min at different temperatures (450～800 ℃) and the combustion products were collected. The morphologies and particle size of detonation soot and that heated at different temperatures were observed by transmission electron microscopy (TEM, JEM-100CXⅡ, Tecnai G220 S-Twin). The X-ray powder diffraction patterns were measured by means of a XRD-6000 diffractometer run at 40 kV and 30 A, with a scan speed of 4°/min and a step of 0.02° using Cu K_α, X-rays of 0.145 06 nm wavelength. The optical properties of detonation soot, detonation

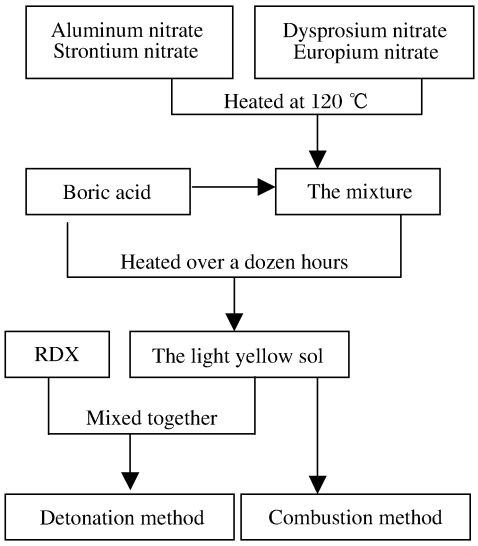
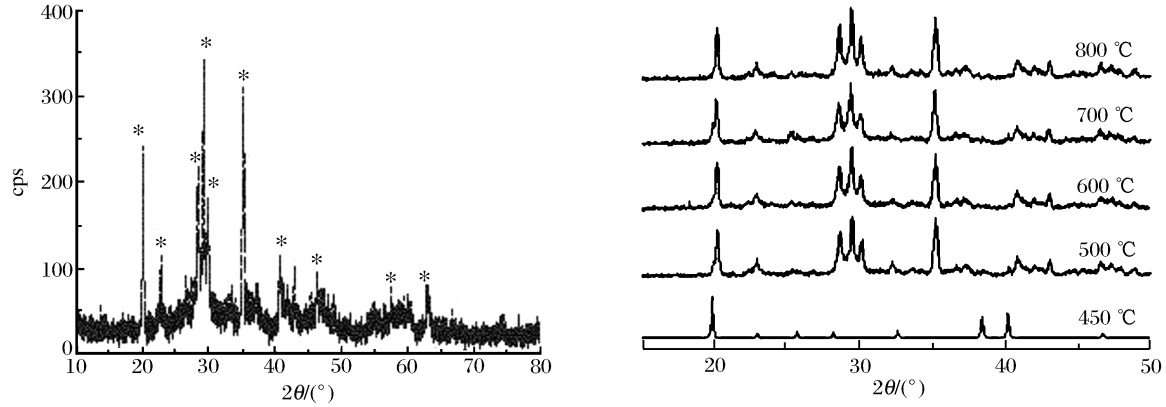


Fig. 1 Schematic flow chart diagram for synthesis of SED nanometer phosphors

soot heated at different temperatures for 1 h and combustion products at different temperatures were studied in a darkroom. All measurements were carried out at room temperature.

2.2 Phosphor Particles Characterization

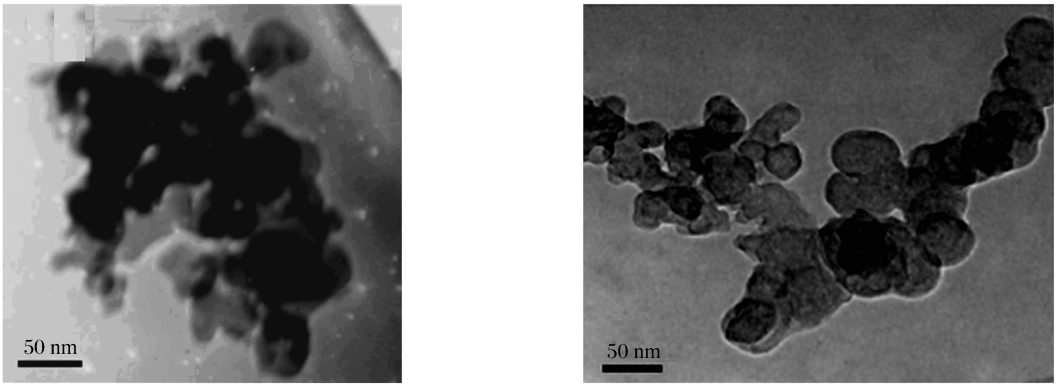
Fig. 2 indicates the XRD patterns of the detonation soot heated at 600 ℃ for 1 h and the SED powders synthesized by combustion method for 5 min at different temperatures. As can be seen from Fig. 2(a), the pattern of detonation soot heated at 600 ℃ for 1 h shows mainly the $SrAl_2O_4$ phase as that described in the JCPDS data (No. 34-0379), which means that the as-prepared SED powders belong to the monoclinic system ($a = 8.442$, $b = 8.822$, $c = 5.160$, $\beta = 93.415$). Meanwhile the as-prepared SED powders prepared by combustion method at 450 ℃ for 5 min has $SrAl_2O_4$ phase, and combustion products at 500～800 ℃ for 5 min show mainly the $SrAl_2O_4$ phase in Fig. 2(b), respectively. The little amount of rare earth ions has almost no effect on $SrAl_2O_4$ phase composition. Normally, $SrAl_2O_4$ has two phases, a high-temperature hexagonal phase (β-phase) and a low-temperature monoclinic phase (α-phase). The transition temperature is around 650 ℃. No other product or starting material was observed, which implies all of the phase compositions of as-prepared particles are all low-temperature α-phase.



(a) Detonation soot heated at 700 ℃ for 1 h　(b) Combustion products at 450～800 ℃ for 5 min

Fig. 2　XRD patterns of the as-prepared SED

The morphologies of the as-prepared SED phosphor powders are presented in Fig. 3. The average size of crystalline can also be calculated according to the Scherrers equation using full-width at the half-maximum data. The results were shown in Fig. 4. The mean particle size obtained from the TEM micrographs was similar to the crystalline size calculated from the XRD patterns. It implied that the obtained phosphor nanoparticles had good crystallinity, which was apparently different from that of the $SrAl_2O_4$ particles obtained from solid-state reaction method. All of the as-prepared phosphor nanoparticles have a slightly larger integral size of aggregates. The aggregate sizes are within the size range for secondary aggregation, however.



(a) Detonation soot heated for 1 h at 700 ℃ (b) Combustion products for 5 min at 700 ℃

Fig. 3 TEM images of the SED nanoparticles

3 Results and Discussion

Fig. 4 shows the average size changes of the as-prepared SED particles at 450～800 ℃. As can be seen, the average size of the detonation soot after annealing at 500～600 ℃ for 1 h increased rapidly than that of the detonation soot after being annealed at 600～800 ℃ for 1 h. Meanwhile the trend of the average size of detonation soot increased with increasing annealing temperature(Fig. 4(a)). While the average size of the combustion products at 500～600 ℃ for 5 min decreased firstly(Fig4. (b)). Then with the increasing of combustion temperature, the average size of the combustion products is also increasing slowly. In the meantime, the average size of detonation soot after thermal treatment is smaller than that of the combustion products at 500 ℃, the average size of detonation soot after thermal treatment is larger than that of the combustion products at the same temperature(600～800 ℃). The main reasons may be associated with that the acting period of shock wave is very short; the crystallites of phosphors prepared by detonation method do no have enough time to grow to large and perfect crystallines. Therefore they have very small article sizes and high density of defects and dislocation[19]. While they were annealed for 1 h at 500 ℃, the high density of defects and dislocation could be lowered greatly to some extent, and the higher specific surface area of the nanosized phosphor powders also attribute to the increasing of the mean size. As for the as-prepared SED particles by combustion, there are many gases formed, such as N_2, NH_3CO_2, NO_x, CO, H_2O which can make the product loose and poriferous. Meanwhile the gases can give a reductive atmosphere. Therefore the mean size can be lowered a lot to some extent.

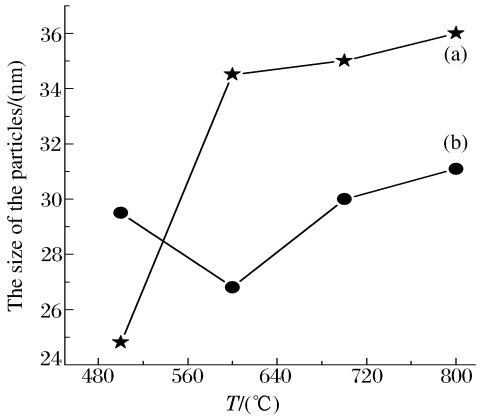


Fig. 4 Average crystallize size in nm as a function of sample annealing temperature
((a) Detonation soot and that heated at different temperatures for 1 h;
(b) Combustion products at different temperatures for 5 min)

Detonation soot heated at 600 ℃ and the SED phosphors synthesized by combustion method at 450～800 ℃ for 5 min were put into a darkroom to study the optical properties. They can emit pea green light after being excited under UV lights. All of them have the shorter afterglow lifetime and

lower brightness,however. The detonation soot heated at 600 ℃ for 1 h has higher brightness than any one else. The SED phosphors synthesized by combustion method at 600 ℃ for 5 min have higher brightness than that synthesized by combustion at other temperature,5 min. This may be associated with the lower content of Eu^{2+} in SED phosphors synthesized by combustion method. The detonation soot heated at 600 ℃ for 1 h can emit higher light. It may have been associated with $Eu^{2+}\rightarrow Eu^{3+}$, when detonation soot is exposed to atmosphere. Meanwhile the SED particles may result in the excessive decreasing of defects because of the quantum size effect of the nanometer phosphors,for example the phosphor particles are so small that Eu^{2+} and Dy^{3+} ions can transferred rapidly into the $SrAl_2O_4$ crystal lattice during heat-treatment process,a lot of defects dispersed on the surface of the 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,the smaller particles made the phosphor crystallize easily and completely,which decreased in the amount of defects in the inner phosphor,and thus lowered the relative intensity of afterglow[17].

As for the detailed reasons and how to improve the afterglow lifetime and brightness of SED nanometer powders,it needs to be further study. Meanwhile why is the SED still a low-temperature monoclinic phase (α-phase) when the temperature increases to 700 ℃,even 800 ℃? It is inconsistent with the fact that nanomaterials normally have the lower melting-point. For example,the melting point of gold is 1 337 K,but that of the ultrafine gold particles of 2.0 nm is lowered to 600 K. In the meantime,in order to further explore a synthesis method fit for the preparation of SED nanometer phosphor powders in quantity,it still needs to study on how to improve the afterglow lifetime and brightness of SED nanometer powders for detonation method. For instance,lowering the content of the carbon may settle the problem by means of using the special-made explosives,or by adjusting the detonation parameters. Meanwhile,it is necessary to improve the dispersion of the SED powders and solve the agglomeration problem. Further work is to be conducted to get a definite understanding. The relevant research is under progressing.

4　Conclusions

The nanosized SED powders belonging to monoclinic system ($a=8.442$,$b=8.822$,$c=5.160$,$\beta=93.415$) can be synthesized both by detonation method,followed by heating the detonation soot at 600 ℃ for 1 h, and by combustion at 500～800 ℃ furnace temperature for 5 min. Compared with the solid-state reaction method and sol-gel method,synthesis temperature of the two methods can be lowered by about several hundred degrees. After being excited under UV lights,all of the as-prepared SED particles can emit pea green light. But the brightness of the SED is sill lower than that synthesized by the solid-state reaction method. The afterglow lifetime is shorter than that synthesized by the solid-state reaction method. Meanwhile,the mean size of SED nanometer phosphor powders prepared by detonation method increased more quickly than that of SED nanoparticles prepared by combustion method at the same annealing temperature,and the mean crystallite size of combustion product had a minimal value at 600 ℃.

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爆轰和燃烧法合成 $SrAl_2O_4:Eu^{2+}, Dy^{3+}$ 纳米发光粉

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摘要: 在低温条件下分别用爆轰法和燃烧法制备出了 $SrAl_2O_4:Eu^{2+}, Dy^{3+}$ 纳米发光粉。从合成条件、热处理温度等方面详细对比了爆轰法和燃烧法对所制备的 $SrAl_2O_4:Eu^{2+}, Dy^{3+}$ 纳米发光粉的晶体生长行为、粒子形貌和光学性质等的影响。研究表明, 随着热处理温度的升高, 爆轰法制备的纳米发光粉的平均粒径逐渐增大, 而燃烧法制备的纳米发光粉的平均粒径先减小后增大, 在 600 ℃ 时平均粒径存在一个极小值。在同样热处理温度下, 爆轰法制备的纳米发光粉的平均粒径增长明显高于燃烧法合成的纳米发光粉的平均粒径。最后讨论了长余辉的发光机理, 并给出了如何改进合成方法的建议。

关键词: 爆轰法; 燃烧法; 纳米发光粉; 光学性质

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