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Synthesis and luminescence properties of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ hollow microspheres via a solvothermal co-precipitation method

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Abstract: $SrAl_2O_4:Eu^{2+},Dy^{3+}$ hollow microspheres were successfully prepared through a facile and mild solvothermal co-precipitation combining with a postcalcining process. The structure and particle morphology were investigated by X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM) pictures, respectively. The mechanism for the formation of spherical $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor was preliminary presented. After being irradiated with ultraviolet (UV) light, the spherical phosphor emitted long-lasting green phosphorescence. Both the photoluminescence (PL) spectra and luminance decay, compared with that of commercial bulky powders, revealed that the phosphors had efficient luminescent and long lasting properties. It was considered that the $SrAl_2O_4:Eu^{2+},Dy^{3+}$ hollow microspheres had promising long-lasting phosphorescence with potential scale-dependent applications in photonic devices.

Keywords: $SrAl_2O_4:Eu^{2+},Dy^{3+}$; hollow microsphere; luminescence; long-lasting phosphor; rare earths

Eu^{2+}, Dy^{3+} co-doped strontium aluminate phosphors have attracted much attention due to their excellent properties such as high initial luminescent intensity, suitable emitting color, long afterglow as well as good stability compared to sulfide phosphorescent phosphors[1–3]. These properties make long persistent phosphors potential material to be applied as luminous paints in highway, airport, buildings and ceramic products[4,5].

Conventionally, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors could be synthesized by solid-state reaction, which often needs a high calcining temperature up to 1400 ℃ to get a single phase[6,7]. This synthesis method often results in inhomogeneous products with low surface area and broad particle size distribution[8]. In recent years, many researchers have devoted themselves to obtain the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors with various methods. Different researches on this aspect have already been carried out and reported. Peng et al.[9] fabricated $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors by combustion synthesis processing, along with heating the resultant combustion ash precursor powder at 1100 ℃ in a weak reductive atmosphere of active carbon. Using aluminum isopropoxide and strontium acetate as precursors, Lu et al.[10] have successfully prepared $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors by a new sol-gel method.

Compared with other methods, solvothermal co-precipitation process is simple, energy saving and the final product with excellent luminescent properties shows smaller particle size and better distribution[11]. Recently, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors have been produced in the form of flakiness[12], particle shape[13] and tubular shape[14]. But to the best of our knowledge, $SrAl_2O_4:Eu^{2+}$, Dy^{3+} hollow spheres phosphors have rarely been reported to date because of the great difficulty in finding an effective synthetic route. Due to the structural advantages, hollow materials have many potential applications in the fields such as photonic device, drug delivery, active-materials protection, and catalysis. Such hollow spheres of rare-earth-doped phosphors can reduce the consumption of expensive rare-earth metals in the synthesis. Additionally, owing to the low density of hollow spherical materials, the phosphors can be well dispersed, thereby enhancing the uniformity and packing density of a phosphor coating[15].

In this paper, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ hollow microspheres were prepared by using a solvothermal co-precipitation method. In the experiment, acetate was used for the raw materical, PVP was chosen as the shape-directed agent and ethylene glycol was elected as the reaction medium. The phase structure, surface morphology, photoluminescence (PL) and afterglow characteristics were studied. Electron microscopy pictures indicated that the final products with the particle size of 2–3 μm could retain the hollow spherical morphology of the precursors. A phenomenological growth mechanism for the microspheres

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was also proposed. Compared with commercial bulky powders, the $SrAl_2O_4:Eu^{2+},Dy^{3+}$ hollow microspheres had promising long-lasting phosphorescence with potential scale-dependent applications in photonic devices. This synthetic route was also suitable for fabricating aluminate phosphors.

1 Experimental

1.1 Synthesis of spherical $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors

$Sr_{0.97}Al_2O_4:Eu^{2+}_{0.01},Dy^{3+}_{0.02}$ phosphors had been prepared by calcining the precursors obtained from solvothermal process at the temperature of 1100 ºC in a weak reductive atmosphere of H_2. $Sr(CH_3COO)_2{\cdot}1/2H_2O$, $Al(OH)(CH_3COO)_2$, $Eu(CH_3COO)_3$ and $Dy(CH_3COO)_3$, polyvinyl pyrrolidone (PVP), $CO(NH_2)_2$, ethylene glycol, all in analytical purity, were used as the starting materials. In a typical procedure, 0.097 mol of $Sr(CH_3COO)_2{\cdot}1/2H_2O$, 0.02 mol of $Al(OH)(CH_3COO)_2$ and 0.04 mol of $CO(NH_2)_2$, 6 g of PVP was dissolved into 90 ml ethylene glycol in a beaker, the solution was stirred at room temperature, then 1 mol.% $Eu(CH_3COO)_3$ and 2 mol.% $Dy(CH_3COO)_3$ were added into the above solution, respectively. After the mixed solution was stirred completely, the mixture was under ultrasonic dispersion for 10 min and transferred into a 50 ml teflon-lined stainless steel autoclave, which was sealed at 200 ºC for 12 h. After the autoclave cooled to temperature, the products were washed with water and ethanol for several times and dried at 60 °C for 24 h.

The $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors were obtained by sintering precursors in a weak reductive atmosphere of H_2 at different temperatures (1050–1200 °C) for 4 h. The heating rate of calcination was 5 °C/min.

1.2 Characterization

The structures of the products were examined by X-ray diffraction (XRD) patterns obtained on a Bruker AXS D8 Focus X-ray diffraction (Cu target, working voltage 40 kV, working current 40 mA, λ=0.15418 nm, slit: 1.0 mm, scanning step length 0.02°, scanning speed 0.1 (°)/min, scanning angle from 10° to 80°). The morphologies of the powders were observed by employing scanning electron microscopy (SEM, Philips XL-30). Photoluminescence (PL) excitation and emission spectra were recorded with a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source, with a slit width of 2.5 and 2.5 nm for excitation and emission, respectively. The thermoluminescence (TL) spectra were measured by FJ-427A1 (Beijing Nuclear Instrument Factory) in the temperature range 303–513 K at a heating rate of 2 K/s. All measurements were carried out at room temperature.

2 Results and discussion

2.1 X-ray diffraction patterns

Fig. 1 gives XRD patterns of the precursor and $SrAl_2O_4:Eu^{2+},Dy^{3+}$ samples prepared at various temperatures for 4 h in a weak reductive atmosphere of H_2. As can be seen from Fig. 1, the diffraction peaks of the precursors are mainly composed of two phases, $SrCO_3$ (JCPDS Card 05-0418) and AlOOH (JCPDS Card 83-2384). After the precursor is sintered at 1050 ºC, the $SrAl_2O_4$ phase has appeared. However, there are still some other phases when the calcining temperature is lower than 1100 ºC, such as $SrAl_4O_7$. The single-phase $SrAl_2O_4$ can be obtained when the calcining temperature is up to 1100 ºC, and the XRD pattern matched well with the PDF standard card (No. 74-0749). Furthermore, according to the XRD phase analysis in Fig. 1, the XRD pattern did not change much both in number and in intensity of the peaks with rising calcination temperature, the doped Eu^{2+} and co-doped Dy^{3+} ions have a little influence on the structure of the luminescent materials.

2.2 Morphology of the precursors and $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphors

The morphologies of the precursors and the products were observed by SEM and TEM. Fig. 2(a) and (b) as well as Fig. 2(c) show typical SEM images and TEM image of solvothermal precursors at 200 ºC, revealing that the precursors consist of separated hollow spheres with diameter of 2–3 μm. By sintering the precursor in a reductive atmosphere of H_2 at 1100 ºC for 4 h, we obtained pure $SrAl_2O_4$ samples in terms of the XRD pattern. The shape and size of these samples are given in Fig. 2(d) and (e) as well as Fig. 2(f), which revealed that the spherical $SrAl_2O_4$ samples had uniform size distribution with an average diameter about 3 μm. It can be known that urea is necessary to produce $SrCO_3$ and AlOOH precipitations[16]. The hydrolysis of urea is the rate control

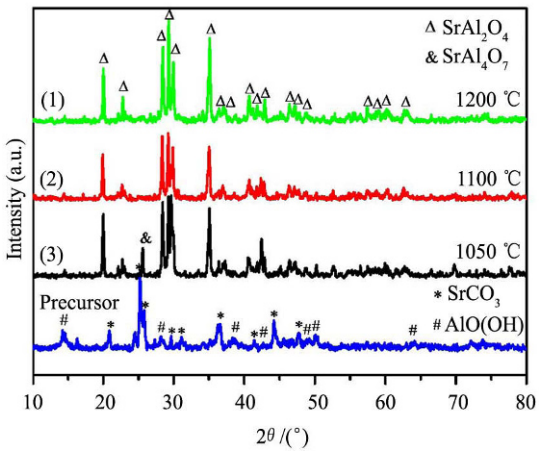

Fig. 1 XRD patterns of the precursor and $SrAl_2O_4:Eu^{2+},Dy^{3+}$ samples prepared by sintering the precursor at 1050 ºC (1), 1100 ºC (2) and 1200 ºC (3)