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A novel approach for preparation of $Sr_3Al_2O_6:Eu^{2+}$, Dy^{3+} nanoparticles by sol–gel–microwave processing

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ABSTRACT

Red long afterglow $Sr_3Al_2O_6:Eu^{2+}$, Dy^{3+} (S3A2O-ED) nanopowders have been prepared by using the conventional sol–gel process and the microwave heating technique. XRD confirmed a cubic $Sr_3Al_2O_6$ single phase for the phosphors. The phosphor powders have a rod-like morphology with little aggregation and the nanorods with diameters of about 80 nm and lengths of about 1 μm. The S3A2O-ED phosphors exhibited a broad excitation band chiefly in visible range and a red broad emission band of main peak at 612 nm under the excitation of 473 nm. Especially the S3A2O-ED phosphors prepared in 20 min of heating time at 680 W exhibited the strongest luminescent intensity and longest decay time.

1. Introduction

Recently, strontium aluminate phosphors activated by europium have attracted much attention since they show excellent properties, such as high quantum efficiency [1], long persistence of phosphorescence and good stability [2,3] when compared with sulfide phosphorescent phosphors. These properties result in a wide application of the materials in many fields [4].

Sol–gel process is an efficient technique for the preparation of the phosphors due to the good mixing of starting materials and relatively low reaction temperature resulting in more homogeneous products [5–8].

Microwave irradiation as a heating method has been found and developed a number of applications in chemistry and ceramic processing [9,10]. Compared with the usual methods, microwave synthesis has the advantages of shortening reaction time, small particle size and high purity.

In recent years, the different phases of strontium aluminate doped with the rare earths have been developed like $Sr_2Al_6O_{11}:Eu^{2+}$, $Sr_4Al_{14}O_{25}:Eu^{2+}$ [11], $SrAl_2O_4:Eu^{2+}$ [12,13], $SrAl_{12}O_{19}:Eu^{2+}$, $SrAl_4O_7:Eu^{2+}$ [14,15], etc. These phosphors are known as efficient green and blue emitters and for their long persistent properties. The calcining temperature and ratio of Al/Sr play an important role in different phase formations in strontium aluminate ($SrO–Al_2O_3$) system. Different studies on this aspect have already been carried out and reported. The phases reported are $Sr_3Al_2O_6$ along with $SrAl_2O_4$ and $SrAl_4O_7$ [16]. The new phase $Sr_3Al_2O_6$ is also seen by Liu [17]. And Akiyama [18] has reported this phase at1300 °C.

The purpose of this paper is to synthesize a red long afterglow S3A2O-ED nanoscale powders at lower power and in shorter time by combining the sol–gel process and the microwave heating technique in a reducing atmosphere. The phase compositions, luminescent properties and the preparation conditions of the sol–gel–microwave method were investigated. The synthesis of S3A2O-ED was seen to be greatly accelerated by microwave heating in our study.

2. Experimental

$Sr(NO_3)_2$, $Al(NO_3)_3·9H_2O$, Eu_2O_3 (99.99%) and Dy_2O_3 (99.99%) were used as the starting materials in the sol–gel route. The analytical grade strontium nitrate and aluminum nitrate were dissolved in deionized water. Eu_2O_3 and Dy_2O_3 were dissolved with dilute nitric acid. The above four nitrate solutions were mixed according to the nominal composition of $Sr_3Al_2O_6:Eu_{0.2}$, $Dy_{0.1}$. Deionized water and glycol were used as the solvent and polymerizing agent for the process. The molar ratio of glycol and total metal cations equaled to 1:1. Homogenous colorless solution was obtained after continuous stirring for 1 h. After adding glycol into the clear solution, the mixture solution was continuously stirred and was adjusted using aqua ammonia. By keeping the solution at 90 °C for 3 h under constant stirring, the solution became viscous. When the sol was dried at 100 °C for 48 h, white dried-gel particles were obtained. These dried-gel particles were placed in a small alumina crucible inside a large covered alumina

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crucible. The space between the small and the large crucible was filled with powdered Fe_3O_4 and active carbon as heating medium and reducing agent [19]. Then the crucibles were placed in a domestic microwave oven (Model Galanz, WP800TL23) with a microwave frequency of 2.45 GHz [9]. These dried-gel particles were calcined in microwave oven for 10–25 min heating time at 680 W of microwave power output in a reducing atmosphere of active carbon to crystallize and form the luminescent centers. Then, the S3A2O-ED phosphor powders were obtained.

The phase of the heat-treated particles was identified by X-ray diffraction (XRD, Rigaka D/Max 2500v/pc, Japan). The morphology and size of phosphor powders were observed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). The photoluminescence spectra were recorded using a fluorescence spectrophotometer (WGY-10). The decay time of afterglow was measured using the brightness meter (ST-86LA) after the samples were sufficiently excited for about 10 min.

3. Results and discussion

Fig. 1 shows the XRD patterns of the S3A2O-ED powders prepared by sol–gel-microwave heating method for different heating times from 10 min to 25 min at 680 W of microwave power out. It was found that the XRD patterns of the powders obtained in 10 min and 15 min were $Sr_3Al_2O_6$ and $SrCO_3$ phases. All the diffraction peaks of the obtained powders in 20 min could be indexed on the cubic system (Space Group: Pa3) of $Sr_3Al_2O_6$ (JCPDS data base No. 24-1187). When the heating time increased to 25 min, some peaks of new phases such as $SrAl_2O_4$, were identified from the XRD pattern. The XRD results demonstrate that a good $Sr_3Al_2O_6$ crystallization could be obtained in only 20 min with microwave heating, compared with conventional sol–gel high-temperature oven heating at 1200 °C for 2 h [5]. The sol–gel–microwave method decreased the heating time greatly.

Fig. 2 shows the FE-SEM micrographs of S3A2O-ED powders obtained for different heating times at 680 W. The powders heated in 10 min in Fig. 2(a) show whisker-like shape and the aggregation was serious. In Fig. 2(b), SEM observation of the powders prepared in 20 min indicates that the powders had a rod-like morphology with slight aggregation and the nanorods with diameters of about 80 nm and lengths of about 1 μm. With increasing heating time, up to 25 min in Fig. 2(c), the aggregation of the sample was serious, and the shape of the phosphor particle was irregular. Furthermore the particle size was in a wide distribution.

Fig. 3 shows the excitation spectra and emission spectra of the S3A2O-ED powders heated for different heating times. It is clearly seen that the excitation spectra of samples had the same peak positions (see Fig. 3(1)). The broad excitation spectra of Eu^{2+} ions were found in the S3A2O-ED powders from 400 to 550 nm for different heating times. As we have known, the excitation transition was considered to be the $4f^7 \rightarrow 4f^6 5d$ of Eu^{2+} with a broad-featured spectrum in the visible light range, when the host material has stronger crystal field strength [20]. The powders heated for 20 min possessed a wide excitation spectrum and the strongest excitation intensity in the visible light region, in comparison with the other powders.

In Fig. 3(2), the emission intensities of the samples increased with the heating time under an excitation of 473 nm. The highest emission intensity was observed with the sample heated for 20 min. With the excited wavelength at 473 nm, the powders exhibited the red light emission spectra within the range of 550–700 nm with the main emission peak at 612 nm. This red emission has a broad-band feature, belonging to the emission of the $5d \rightarrow 4f$ transition of Eu^{2+} ions [21,22] in $Sr_3Al_2O_6$.

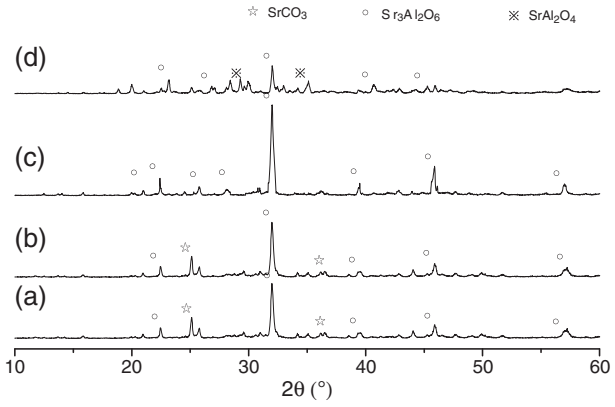

Fig. 1. XRD patterns of S3A2O-ED powders heated with microwave at 680 W for (a) 10 min, (b) 15 min, (c) 20 min, and (d) 25 min.

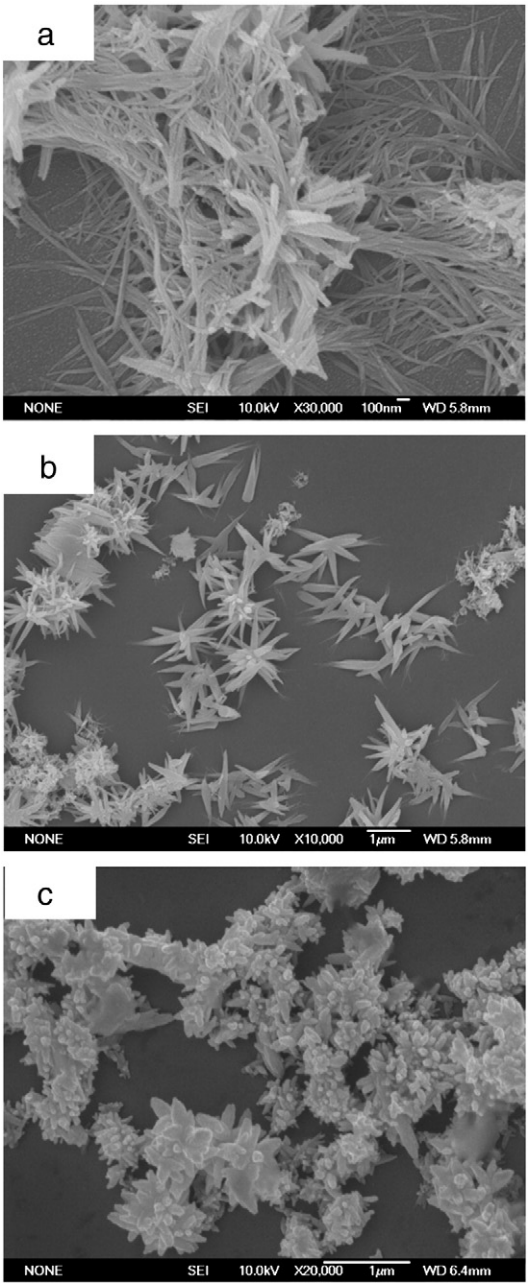

Fig.2. FE-SEM micrographs of S3A2O-ED powders heated with microwave at 680 W for (a) 10 min, (b) 20 min, and (c) 25 min.