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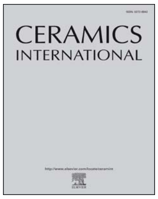

Preparation and properties of Eu and Dy co-doped strontium aluminate long afterglow nanomaterials

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ABSTRACT

The long afterglow nanomaterials of strontium aluminate co-doped by Eu and Dy have been synthesized by co-precipitation combined hydrothermal method. The effects of hydrothermal time, calcination time, pH value, the amount of aluminum nitrate, activator, co-activator and flux H_3BO_3 on the fluorescence properties of the product were investigated by means of single factor optimization experiment. Then the orthogonal experiment was employed to obtain the optimal synthesis conditions that are as follows: $n_{Dy}/n_{Eu} = 2.5$, $t_c = 2.5$ h, $n_{Eu}/n_{Sr} = 0.02$, $t_h = 8$ h. Subsequently, the optimal synthesis conditions were verified by three repeated experiments, and the obtained products were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and fluorescence spectrometer. The results showed that the synthesized target products all were the mixed crystal phase of $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$. The particles presented regular spherical-like with size ~ 100 nm. The dopants Eu and Dy were confirmed existed in the $SrAl_2O_4$ powders. The fluorescence and afterglow data of the target products were better than that in the orthogonal experiment scheme. The primary emission spectra band was in the range of 400–600 nm with characteristic peak located at ~ 460 nm corresponding to the transitions of Eu^{2+} ions from $4f^65d \rightarrow 4f^7$, and the blue light can be observed by naked eyes. The similar fast-decaying and slow-decaying processes were displayed in all the afterglow curves, and the initial afterglow brightness of the target product is apparently higher than that of products synthesized by the orthogonal experiment. The synthesized target products, which show excellent long afterglow performance, present a great application prospects in the aspects of ceramics, plastics, arts and crafts, ink and coating.

1. Introduction

Rare earth doped inorganic luminescence materials have been applied to lots of fields including industrial lighting, radiation dose measurement, color display and other realms. Their fluorescence can be maintained for several hours, and they are difficult to be decomposed upon exposure to ultraviolet radiation or wet gas. Meanwhile, this material is environmentally friendly. Thus, the conventional phosphors have been gradually replaced by RE metal-doped phosphor. Among rare earth doped inorganic phosphors, long afterglow aluminates phosphors were vigorously developed, since their afterglow lifetime and brightness were 10 times higher than that of traditional sulfide emitters, and various colors light could be emitted stably and efficiently. In particular, rare earth doped strontium aluminates have attracted great attention as a new type of long afterglow luminescence material. Its luminescence is due to the transition of Eu^{2+} ions from $4f^65d \rightarrow 4f^7$. Compared with the traditional sulfide based phosphors, this long afterglow luminescence material exhibits lots of merits, such as long luminescence time, high luminescence intensity and quantum efficiency, stable luminescence performance, no radiation and so on.

At present, these rare earth doped strontium aluminates are prepared chiefly by solid-state reaction. Due to its high sintering temperature, the disadvantageous properties of the target products, like large particle size, nonuniform size distribution and low luminescence efficiency significantly after milling, are difficult to be controlled. Therefore, considerable new synthetic approaches have been successfully introduced to this material synthesis in recent years. Sol-gel method [1] whose ignition temperature is obviously lower than that of solid-state reaction, meanwhile, the phase and size of the prepared target product are even. Combustion method [2] whose reaction time needed is short as well as temperature is low, so the energy-saving effect is obvious. Co-precipitation method [3] whose particle size is small

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and even, and product distribution is well. Hydro-thermal method [4] is a highly effective synthetic method, and the reaction conditions are mild, the products from this method have even phase and high purity as well as good crystallinity, stable performance at high temperature. Micro wave method [5] whose experiment equipment is simple and easy to operate, the products obtained from this method are crumbly and easy to grind.

Herein, we prepared long afterglow nanophosphors co-doped with Eu^{2+}, Dy^{2+} through combining the hydrothermal and co-precipitation methods. Meanwhile the influences of hydrothermal time, calcination time, pH value, the amount of aluminum nitrate, activator, co-activator and flux H_3BO_3 on the fluorescence properties of the product were systematically investigated by means of single factor optimization experiments. Whereafter, based on the single factor optimization experiments, the orthogonal experiment scheme was employed to further optimize the primary effecting factors, and the optimal preparation conditions were obtained. Subsequently, the target products was prepared under the obtained optimal conditions, and analyzed by means of XRD, SEM, EDX, and fluorescence spectrometer.

2. Experimental

2.1. Chemical reagent

Europium oxide [Eu_2O_3, 99.99%], dysprosium oxide [Dy_2O_3, 99.99%], aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$ (AR)], urea [NH_2CONH_2 (AR)], nitric acid [HNO_3 (GR)], polyethylene glycol 200 [HO $(CH_2CH_2O)nH$ (CP)], boric acid [H_3BO_3 (GR)], granular activated carbon (AR), strontium nitrate[$Sr(NO_3)_2$ (AR)], ammonium carbonate [$(NH_4)_2CO_3$ (AR)], absolute alcohol (≥ 99.7%).

2.2. Experimental instrument and measurement method

X ray diffraction (XRD) analysis: The phase detection of the target products was obtained from Shanghai International Trade Co. Ltd XRD-6100 polycrystalline powder X ray analyzer (Cu Kα radiation); tube voltage 40 kV; tube current 30 mA; 2θ angle ranges from 10 to 80 with a step of 0.02 and counting time of 4°/min.

Scanning electron microscope (SEM) analysis: The electron microscopy of the target products was measured by F20 SEM (model Tecnai G^2 F20 S-TWIN, the United States FEI). The preparation of the sample was as follows: a trace amount of target products were dispersed in ethanol and was evenly mixed, then the mixture was dropped with a dropper to the prepared copper grid, and was dried to conduct experiment.

Energy-dispersive X-ray spectroscopy (EDX) analysis: The elemental analysis was carried out using an energy dispersive X-ray spectrometer with an excitation electron beam at accelerating voltage of 20 kV.

Fluorescence spectrum analysis: The solid fluorescence was measured by HITACHI F-2700 fluorescence spectrometer (operation voltage 400 V, with a slit width of 5 nm).

Afterglow lifetime analysis: The afterglow lifetime was measured through HITACHI F-2700 fluorescence spectrometer with the xenon lamp as excitation light, a light source with a fixed energy and fixed time was used to excite the product and then closed, then the relationship between the intensity of light emitted by the product and time was detected (operation voltage 700 V, with a slit width of 2.5 nm, scanning speed 0.2 s, scanning length 200 s).

2.3. Solution preparation

2.3.1. Preparation of rare earth nitrate solution

0.1 mol/L $Eu(NO_3)_3$ solution: Stoichiometric ratio Eu_2O_3 was wetted with a small amount deionized water and then magnetic stirred at 60 °C, meanwhile, the concentrated HNO_3 (1/1, *v*/*v*) was added dropwise until the Eu_2O_3 was completely dissolved. Next, the mixture was heated up to 80 °C to evaporate excessive HNO_3 and H_2O until the solution was sticky. Finally, the sticky $Eu(NO_3)_3$ was dissolved with another a certain amount of deionized water, then cooled to room temperature, and transferred to a volumetric flask for constant volume and further use.

The preparation method of 0.1 mol/L $Dy(NO_3)_3$ aqueous solution is similar to that of $Eu(NO_3)_3$.

2.3.2. Preparation of other solutions

1 mol/L $Al(NO_3)_3$ solution: Stoichiometric ratio $Al(NO_3)_3 \cdot 9H_2O$ solid was weighed quickly and dissolved completely in a certain amount of deionized water, then transferred to a volumetric flask for constant volume and further use.

The preparation method of 1 mol/L $Sr(NO_3)_2$ aqueous solution and 2 mol/L $(NH_4)_2CO_3$ water solution are similar to that of $Al(NO_3)_3$.

2.4. Synthetic method

The synthesis method of title product was as follows: In a four-neck flask, urea (2.24 g) was dissolved in deionized water by magnetic stirring at room temperature to form homogeneous solution. Next, PEG-200 (4.96 g) was added under magnetic stirring at 80 °C, followed by Al $(NO_3)_3$ (8 mL) and $Sr(NO_3)_2$ (4 mL) solution were added in turn and kept stirring at constant temperature. Subsequently, a certain volume of $Eu(NO_3)_3$ and $Dy(NO_3)_3$ solution were also added into flask and stirred for 0.5 h to uniform. $(NH_4)_2CO_3$ (over 10%) solution was slowly dropped into the above mixture until the pH value of the mixture reached a certain value. Then the resultant solution was vigorously stirred for 2 h, transferred to a 100 mL hydro-thermal reactor and treated at 170 °C for a period of time. After the reactor was cooled to room temperature, the resultants were filtered and washed for 2–3 times with ethanol and deionized water respectively, and then put into air dry oven to dry for 24 h, a certain proportion flux (H_3BO_3) was added after weighing. Finally, the evenly mixed solution was put into the crucible and was calcinated under 1200 °C in a muffle furnace at a reducing atmosphere provided by activated carbon, and then the product was obtained.

3. Experimental results and discussion

3.1. Single factor optimization of synthesis conditions of the product

The amount of aluminum nitrate is represented by the molar ratio of aluminum nitrate and strontium nitrate n_{Al}/n_{Sr}. The amount of activator is expressed by the molar ratio of europium nitrate and strontium nitrate n_{Eu}/n_{Sr}. The amount of co-activator is shown by the molar ratio of dysprosium nitrate and europium nitrate n_{Dy}/n_{Eu}. Hydro-thermal time is represented by t_h. The amount of flux is expressed by the mass ratio of solid boric acid and resultant precipitation M_B/M_P. Calcination time is expressed by t_c. Calcination temperature is expressed by T_c. Excitation and emission wavelengths are represented by λ_{am} and λ_{em} respectively.

3.1.1. Effect of the amount of aluminum nitrate on the luminescent properties of the product

Fixed $n_{Eu}/n_{Sr} = 0.025$, $n_{Dy}/n_{Eu} = 2$, pH = 8, $t_h = 7$ h, $M_B = 10\%$ M_P, $t_c = 2$ h, $T_c = 1200$ °C, the effect of the amount of aluminum nitrate on the fluorescence properties of product was explored. The fluorescence emission spectra and afterglow decay curves of the product were shown in Fig. 1(a) and Fig. 1(b).

It can be seen from the Fig. 1(a), the fluorescence emission spectrum of products with different n_{Al}/n_{Sr} showed broad-band spectra with single emission peak. The fluorescence intensity of the product gradually increased with the increment of n_{Al}/n_{Sr}, and reached the maximum at $n_{Al}/n_{Sr} = 2$, then gradually decreased. At the same time, the fluorescence emission peaks shift to a blue short wavelength from a green