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Synthesis and characterization of long persistence Sr₄Al₁₄O₂₅ : Eu²⁺, Dy³⁺ phosphor prepared by combustion method

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Eu²⁺, Dy³⁺ co-doped, strontium aluminate (Sr₄Al₁₄O₂₅) phosphors having high brightness and persistent afterglow were prepared via initial combustion at 600 °C, followed by sintering the resultant combustion ash at different temperatures in a reducing atmosphere of 95% N₂ and 5% H₂. Boron oxide and urea were used as flux and reducing fuel, respectively. The luminescence properties were investigated by changing the amount of flux, fuel to oxidizer ratio (F/O) and final sintering temperature. The crystallization and surface characterization of the precursor and target powder were investigated by X-ray diffraction (XRD) and field emission-scanning electron microscopy (FE-SEM). The photoluminescence (PL) properties were studied by using a PL spectrometer. The results showed that the single-phase Sr₄Al₁₄O₂₅ was formed at 1100 °C and dominated as the temperature was increased to 1500 °C, with a bluish-green emission and a maximum peak at 490 nm, which was attributed to the following typical electronic transition of Eu²⁺ : 4f⁶5d¹ \rightarrow 4f⁷. Co-doped Dy³⁺ ions acted as the trapping center by capturing the free holes in the system, thus generating a persistent afterglow. The emission intensity was influenced by the flux amount and the F/O ratio. Nevertheless, the emission intensity and the afterglow time increased with increasing final sintering temperature up to 1500 °C.

Key words: Long phosphorescence phosphor, Photoluminescence, Sr₄Al₁₄O₂₅, Combustion process, After glow.

Introduction

Phosphor with persistent afterglow is a kind of energy storage material capable of easily absorbing both ultraviolet and visible light energy and then gradually releasing the energy as visible light in the darkness at a certain wavelength for a considerable duration. Persistent phosphors have potential application in various fields such as emergency signs, military applications, textile fibers, textile printings, lightening apparatus and switches, exit signboards, luminous paints, glowing watches and toys. [1]. As a result, numerous studies on this kind of long persistence phosphor have been conducted by many researchers. Several decades ago, Co- and Cu-doped ZnS were considered the main phosphorescent materials. However, this material is not chemically stable enough because sulfide absorbs moisture from the surrounding environment which also reduces its afterglow property [1, 2].

In the past decades, research on long persistence phosphors has moved towards aluminates and silicates doped with rare earth ions, in which the metal aluminates or silicates act as a host lattice while the rare earth ions act as emission and trapping centers, respectively. Presently, a few strontium aluminate phosphors activated by Eu²⁺ and Dy³⁺ have attracted much attention due to their excellent properties. Strontium aluminate phosphors have several valuable properties that can be used to overcome the shortcomings of classical sulfide phosphors such as high emission intensity, color purity, chemical stability, safety and radiation-less characteristics. The most commonly used strontium aluminate hosts are SrAl₂O₄ and Sr₄Al₁₄O₂₅. The excitation and emission spectra of Eu^{2+} ions are dependent on the host materials used. which are broadband due to transitions between the $4f^{6}5d^{1}$ excited state and the $4f^{7}$ ground state configurations [4-6]. Here, the transitions of $4fT^65d^1 \rightarrow 4f^7$ are partially allowed, electronic transitions of high probability [3]. As the position of the 5d level of Eu^{2+} depends strongly on the surrounding crystalline environment, the changes in the energy levels between the excited and ground states can vary for the same rare earth ions in different host. Briefly, for the crystal field effect, Eu²⁺can emit various visible lights in different hosts. With Sr₄Al₁₄O₂₅ as a host, Eu²⁺ shows a bluish-green emission at 490 nm. Dy³⁺ ions are co-doped into the lattice, which acts as a hole trapper, thus generating a persistent glow [3, 4].

The phosphors can be synthesized by a variety of routes: solid-state reactions, sol-gel techniques, microwave heating techniques, hydroxide precipitation, an electric arc method, hydrothermal synthesis and combustion synthesis. The combustion process to prepare phosphors is advantageous in its short time processing, safety and energy saving. Moreover, homogeneous mixing is also

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Fig. 1. Flow chart for the preparation of $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} by combustion method and its characterizations.

possible through this process. As a result, this synthesis technique has been extensively applied to prepare various oxide materials [6, 7]. However, not many studies have been performed to examine combustion synthesis on phosphor in detail. In this study $Sr_4Al_{14}O_{25}$ Eu²⁺, Dy³⁺ is synthesized by combustion method in a reducing atmosphere. The effects of flux amount, fuel and final sintering temperature on the luminescence properties are investigated.

Experimental

Sr(NO₃)₂, Al(NO₃)₃ · 9H₂O, Eu₂O₃, Dy₂O₃, B₂O₃ and NH₂CONH₂, all of analytical grade purity, were employed as starting materials. B₂O₃ and NH₂CONH₂ were used as flux and fuel, respectively. Stoichiometric amounts of $Sr(NO_3)_2$, $Al(NO_3)_3 \cdot 9H_2O$, B_2O_3 and NH₂CONH₂ were dissolved in 40 ml of deionized water. Another solution of Eu³⁺ and Dy³⁺ was prepared by dissolving stoichiometric amounts of Eu₂O₃ and Dy₂O₃ in 20 ml of HNO₃ solution. These two solutions were then mixed and stirred for 2 hrs at 70 °C to obtain a homogeneous precursor solution. After complete stirring, the precursor solution was introduced into a box furnace maintained at 600 °C for 5 min. The solutions were boiled, dehydrated and decomposed. Large amounts of gases (oxides of carbon, nitrogen and ammonia) escaped from the reactants and were spontaneously ignited, leading to complete combustion. The whole process was over within 5 min. The voluminous and foamy combustion ash was milled to obtain the precursor powders. Precursor powders were again sintered at 1100 °C-1600 °C in the reducing atmosphere of 5% H_2 + 95% N_2 for 3 hrs in order for different studies to be conducted. Phase identification of the synthesized phosphor powders was carried out by using an X-ray diffractometer (Rigaku D/max-2200/ pc) with Cu-Ka radiation. The morphology of the powders was observed by using a field emissionscanning electron microscope (FE-SEM, Hitachi S-1400). The photoluminescence (PL) spectra and decay curves were obtained using a PL spectrometer (Hitachi, F-4500) with a pulse Xe lamp. The experimental procedure of this study is summarized in Fig. 1.

Results and Discussion

Material characterizations

Fig. 2 shows the X-ray diffraction (XRD) patterns of the precursor powder and the target phosphor sintered at different temperatures. The precursor powders were prepared at 600 °C and the XRD pattern shows the formation of SrAl₂O₄ phase. At 1100 °C, peaks for multiple phases such as SrAl₂O₄ and Sr₄Al₁₄O₂₅ occurred. With increasing temperature, the intermediate phase of SrAl₂O₄ disappeared. At temperatures higher than 1200 °C, only Sr₄Al₁₄O₂₅ phase was found. The XRD pattern indicated that no significant change in the host crystal occurred due to the doping of Eu^{2+} and Dy^{3+} . Generally, it can be assumed that Eu^{2+} and Dy^{3+} ions enter into the Sr^{2+} ion sites in the $\mathrm{Sr}_4\mathrm{Al}_{14}\mathrm{O}_{25}$ host because the radii of Eu $^{2+}$ (1.17 Å) and Dy $^{3+}$ (1.07 Å) ions are similar to that of the Sr^{2+} ions (1.18 Å) [5]. Therefore, their substitutions may not generate a



Fig. 2. X-ray diffraction patterns of $Sr_4Al_{14}O_{25} : Eu^{2+}$, Dy^{3+} ; (a) precursor powder and target powders post annealed at (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1400 °C and (f) 1600 °C.



Fig. 3. SEM micrographs of $Sr_4Al_{14}O_{25}$: Eu^{2+} , $Dy3^+$; (a) precursor powder and target powders post annealed at (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, and (e) 1400 °C.

significant distortion of the lattice parameter. It is possible for B³⁺ (0.02 nm) ions to enter into the Al³⁺ ion sites or any interstitial sites in the Sr₄Al₁₄O₂₅ host. If a B³⁺ ion substitutes into an Al³⁺ ion site, the principal peak should be shifted toward a higher value since the radius of B³⁺ (0.27 Å) is smaller than that of Al³⁺ (0.535 Å). This explains the slight shift towards to the left of the principle peak of Sr₄Al₁₄O₂₅ in Fig. 1. We therefore concluded that the B³⁺ ions probably occupied the interstitial sites in the Sr₄Al₁₄O₂₅.

Fig. 3 shows SEM micrographs of the synthesized precursor powder and post annealed phosphor powders heated at different temperatures. The surface of the precursor powder shows many pores, which was attributed to the escape of various gases such as NO_x, CO_x, and NH₃ during the combustion reaction between the precursor nitrates and urea. The irregular gain size and low crystallinity of the precursor powder are due to the low firing temperature and rapid combustion reaction. We assumed that particle coalition occurred at the high-heat treatment temperature. The SEM micrographs show the irregular shape of the particles with a mixture of different shapes at lower sintering temperature, but at higher temperature a hexagonal shape with a particle size of about 2-3 µm dominated. This was attributed to the rapid combustion process, and non-uniform distribution of the temperature and mass flow in the combustion flame [7].

Photoluminescence (PL) properties

In the host lattice of $Sr_4Al_{14}O_{25}$, Eu ions can be stabilized in either divalent (Eu²⁺) or trivalent (Eu³⁺) oxidation state. The incorporation and stabilization of Eu ions in the sample were confirmed by the luminescence investigations. Fig. 4 shows the PL spectrum of $Sr_4Al_{14}O_{25}$: Eu^{2+,} Dy³⁺. The spectrum shows that excitation occurred through a broad band from 220 nm to 490 nm with the maximum peak at 369 nm and that a broadband greenish-blue emission originating from Eu²⁺ was accompanied with the



Fig. 4. Excitation and emission spectra of $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} phosphor sintered at 1300 °C.



Fig. 5. Emission spectra of $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} phosphors sintered at different final temperature.

maximum peak at $\lambda = 493$ nm, which is in good agreement with other reports [2, 3, 8]. The intense excitation observed in the UV region is associated with the 4f- 5d electronic transition [3, 4].

The sintering temperature significantly affected the emission intensity. Fig. 5 shows that the emission intensity considerably increased as the temperature was increased within the range from $1100 \,^{\circ}$ C to $1500 \,^{\circ}$ C.

This result is also in good agreement with other studies [5, 7, 9, 10]. The PL intensity of the phosphor increased monotonically with increasing annealing temperature. The stronger PL intensity observed at the higher sintering temperature was attributed to the good activation of Eu^{2+} , the increased particle size and the high crystalline of the host lattice [7, 10]. At temperatures higher than 1500 °C, phase transformation occurred with a change of emission peak maxima at 510 nm. At 1600 °C, the emission intensity decreased, which was attributed to the phase transformation and the occurrence of partial melting.

The effect of flux on the synthesis process and luminescence properties is also an important factor in luminescence study. Some studies reported on the optimum amount of flux required to obtain a good emission spectrum for aluminate luminescence material doped by rare earth metals [11, 12]. In this study, we used B₂O₃ as flux. Although the action and mechanism of B₂O₃ remain unclear, it is believed that flux exerts a considerable effect in reducing atmosphere during the sintering process, improves crystalline properties [13], and increases oxygen vacancies in the host lattice [4], thereby improving the phosphorescence property. Fig. 6 shows the steep increase in emission intensity as the flux content was increased up to 0.5 mol, after which it suddenly dropped with further increase of flux content. The optimum flux was therefore considered to be 0.5 mol with respect to the host composition.

Fig. 7 shows the emission intensity of the sample as a function of oxidizer to urea (F/O) ratio. Five F/O ratios (0.5, 1.0, 1.5, 2.0, and 2.5) were used to determine the effect of urea on luminescence properties. At an F/ O ratio of 1.5, the $Sr_4Al_{14}O_{25}$: Eu²⁺, Dy³⁺ phosphor generated the highest emission intensity due to optimized heat release. With increasing F/O ratio, the emission intensity began to drop again because the excessively high urea concentration induced a large heat release, which is not favorable for forming the $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} single-phase monoclinic structure [14, 15]. On the other hand, a lower urea concentration provides a lower reactive temperature, which results in incomplete reaction of raw materials. According to the figure, the optimal F/O ratio is 1.5 times higher than the theoretical quantity of 1.0, in order to obtain a good initial luminescence of the $Sr_4Al_{14}O_{25}$: Eu²⁺, Dy³⁺ phosphor.

Fig. 8 shows the afterglow decay curves of the $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} phosphors prepared by combustion method as a function of heat treatment temperature. Before the spectrum was measured, the phosphor samples were exited by Xe lamp for 5 min. The heat treatment temperature clearly exerted a significant effect on the initial luminescence intensity and afterglow decay rate. With increasing heat treatment temperature, the initial luminescence intensity increased and the decay rate decreased.



Fig. 6. Emission intensity of $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} phosphor sintered at 1300 °C with various flux contents.



Fig. 7. Emission spectra of $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} phosphor sintered at 1300 °C with various urea ratios.



Fig. 8. Emission spectrum of $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} phosphor prepared at different sintering temperature.

It is well established that in $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} phosphor, Eu^{2+} ions act as a luminescence center [5] and the bluish green emission is attributed to the electronic transition from the 5d level to the 4f level of the Eu^{2+} ions. Dy^{3+} ions are considered to play a key role in long afterglow property and are assumed to take a position in between the ground state and the excited state of the Eu^{2+} ions [4]. When phosphors are excited, the electrons of an Eu^{2+} ion in the 4f level transfer to

the 5d level, while holes are produced in the valence band. Some of these holes are captured by Dy^{3+} hole traps, which are slowly released to the valence band. Consequently, the holes from Dy^{3+} trapping and the elections released from excited 5d levels of Eu^{2+} are recombined, leading to the emission of persistent bluish green light.

Conclusion

 $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} phosphor was successfully prepared by combustion method. The analytical results indicated that this phosphor has a main emission peak at 490 nm with bluish green emission. A single phase of $Sr_4Al_{14}O_{25}$: Eu^{2+} , Dy^{3+} formed at heat treatment temperatures above 1200 °C, whereas a second phase of SrAl₂O₄ occurred both at lower (less than 1200 °C) and higher temperatures (more than 1500 °C). The amount of B₂O₃ flux significantly affected the emission intensity and the optimum amount was determined to be 0.5 mol with respect to the host composition. The experimental results showed that the optimal F/O ratio is 1.5 times higher than the theoretical ratio. With increasing heat treatment temperature, the emission intensity of the phosphor increased, and the initial intensity of the decay curve increased, but the decay speed decreased, i.e., the afterglow time increased.

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