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Photoluminescence properties of $SrAl_2O_4$ and $CaAl_2O_4$ long-phosphorescent phosphors synthesized by an oxalate coprecipitation method

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Long phosphorescent oxide phosphors have been synthesized through an oxalate coprecipitation method. For stoichiometry, the precipitates of hydroxyoxalates including metal ions were obtained at pH 10. Phosphorescent phosphors, "SrAl₂O₄:Eu, Dy" and "CaAl₂O₄:Eu, Nd", were prepared by an oxalate co-precipitation method under a reducing atmosphere, showed the peaks of crystalline phases in XRD patterns. The photoluminescence spectra of the long phosphorescent phosphors were analyzed. For the excitation wavelength of 365 nm and 254 nm, the phosphors, SrAl₂O₄:Eu, Dy and CaAl₂O₄:Eu, Nd exhibited emission spectra around 514 nm and 476 nm, which are caused by the 5d-4f transition of the Eu²⁺ ions, respectively.

Key words: Long phosphorescent phosphor, SrAl₂O₄, CaAl₂O₄, Oxalate coprecipitation method, Photoluminescence.

Introduction

Phosphorescent phosphors have great potential in several applications for devices and luminous paints and have been widely studied. A phosphorescent material such as the ZnS matrix has been well known as a longlasting phosphor but did not show sufficient brightness and long phosphorescent behavior [1, 2]. The chemical instability and fast luminance change of such a sulfide material has been proposed as the problems in practical applications.

 Eu^{2+} -doped alkaline earth aluminates, MAl₂O₄: Eu^{2+} (M: Ca, Sr, Ba) phosphors with a strong photoluminescence in the blue-green visible range have been studied by many researchers [3, 4]. These materials have important industrial applications with a longpersistence luminescence. Phosphorescent phosphors of the host matrix with spinel oxide materials, SrAl₂O₄ co-doped with Eu^{2+} , Dy^{3+} , $CaAl_2O_4$ co-doped with Eu^{2+} , Dy^{3+} and $Sr_4Al_{14}O_{25}$ co-doped with Eu^{2+} , Dy^{3+} have been regarded to be useful green and blue phosphors because of their extremely long persistence phosphorescence [5-8]. The phosphorescent phosphors, $CaAl_2O_4$, SrAl₂O₄ hosts belong to the stuffed tridymite structure and the framework consists of AlO4 tetrahedra, with $M^{2\scriptscriptstyle +}~(Ca^{2\scriptscriptstyle +},~Sr^{2\scriptscriptstyle +})$ ions in the cavities to balance the charge [9, 10]. The Sr²⁺ (0.127 nm) or Ca²⁺ (0.112 nm) ions in the cavities are substituted by the activator ions, Eu^{2+} (0.130 nm). $Sr_4Al_{14}O_{25}$ phosphor has an orthorhombic structure, which is built up of alternating strands containing either AlO_6 octahedra or AlO_4 tetrahedra [8-11].

It is known that the persistent luminescence lifetime and intensities of phosphors can be enhanced by codoping with other rare earth ions [12]. The phosphorescence from the aluminates is believed to be caused by the 4f-5d transition of the Eu^{2+} ions in the crystals and this behavior is based on the thermal activation of holes from traps followed by the emission of Eu^{2+} [13, 14]. Such electron transitions have been reported to be affected by the electrical environment around the Eu^{2+} ions. Thus the color of the phosphor is dependent upon the crystal structure of the mother phases.

Several synthesis methods such as a solid-state reaction, a hydrothermal reaction, a sputtering method and a sol-gel method have been investigated [2-4]. The solid-state reaction process has been used intensively for phosphor synthesis, but this process often results in poor homogeneity and requires a high calcination temperature with a prolonged heat treatment. Researche on a sol-gel process for phosphor materials with homogeneity, a stoichiometric composition and a fine grain size have been reported [6, 15]. However, chemical solution methods in preparing phosphors have rarely been investigated and the fabrication conditions have not been well established. A chemical solution method such as an oxalate coprecipitation process, is based on the different solubility of the cation in the oxalate compounds, which requires the precise control of the reaction environment (pH) and the cation stoichiometry in solution for quantitative coprecipitation [16]. Generally, the powder phosphors obtained by coprecipitation

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techniques, have a smaller grain size and are of higher purity and homogeneity than the powders fabricated through a solid-state reaction method.

In this study, the long phosphorescent phosphors, $SrAl_2O_4$:Eu, Dy and $CaAl_2O_4$:Eu, Nd were synthesized by an oxalate coprecipitation method. The optimal reaction conditions to form the precursors from the constituent metal ions were applied for the synthesis of the phosphor materials. The phase analysis and microstructural observations were carried out for these powder phosphors. The photoluminescent characteristics of the long phosphorescent phosphors, $SrAl_2O_4$:Eu, Dy and $CaAl_2O_4$:Eu, Nd were examined in terms of excitation wavelength.

Experimental Procedure

Synthesis of long phosphorescent phosphor powders

The phosphorescent phosphors were synthesized through the coprecipitation reactions of the constituent component ions $(Sr^{2+}, Ca^{2+}, Al^{3+}, Eu^{3+}, Dy^{3+}, Nd^{3+})$ using oxalic acid, $H_2C_2O_4$. The 0.1 M solutions to obtain the precursors were prepared using starting materials; Sr(NO₃)₂ (Junsei, 97%), Al(NO₃)₃ 9H₂O (Junsei, 98%), $Eu(NO_3)_3$ 5H₂O (Aldrich, 99.9%), $Dy(NO_3)_3$ 5H₂O (Aldrich, 99.9%), Ca(NO₃)₂ 4H₂O (Junsei, 98%), Nd(NO₃)₃ 5H₂O (Aldrich, 99.9%). The oxalic acid was added into the solutions, which were adjusted to the level of pH 10 by adding ammonia solution. The solutions were strongly stirred and filtered, and then washed. The precursors, which were obtained by drying the solutions, were calcined at 1000 °C in air. The long phosphorescent phosphors, "SrAl₂O₄:Eu, Dy" and "CaAl₂O₄:Eu, Nd" were obtained through heat treatment in a reducing atmosphere of 5% H_2/N_2 .

Characterization of long phosphorescent phosphor powders

The crystalline phases of the phosphorescent phosphors were identified by X-ray diffraction analysis (XRD, MXP-3, Macscience Co.). The morphologies of the powders synthesized were observed using field emission scanning electron microscopy (FE-SEM, S-4200, Hitachi). The luminescence behaviors of the phosphorescent phosphors, "SrAl₂O₄:Eu, Dy" and "CaAl₂O₄: Eu, Nd" were examined with a spectrofluophotometer (RF-5301, Shimadzu) at room temperature. The photoluminescence spectra of the phosphors, which were synthesized through an oxalate coprecipitation method, were investigated with excitation wavelengths at 365 nm and 254 nm. The intensities of the emission spectra of the phosphorescent phosphors, which were excited at the excitation wavelength, were measured throughout the entire wavelength range of 200 nm to 650 nm.

Results and Discussions

In the synthesis of the phosphorescent phosphors, the coprecipitation of a hydroxide containing an alkali earth metal was achieved above pH 10. However, the stoichiometric precipitates of other metal ions can be formed in the range of pH 5 to pH 10. The stoichiometric coprecipitation of the oxalate including a pure alkali earth metal ion occurs above pH 4. Because the pure oxalates with Al³⁺, Eu³⁺, Dy³⁺, Nd³⁺ ions show a high solubility in solution, it is impossible to form the stoichiometric precipitates in solution. Thus, it can be seen that such metal hydroxyoxalate precipitates rather than a pure oxalate form are suitable to synthesize stoichiometric oxide precursors. Therefore, it was found that the optimum synthesis condition of the stoichiometric precipitates for the oxide phosphors was above pH 10.

Figure 1 shows the XRD patterns of the "SrAl₂O₄: Eu, Dy" and "CaAl₂O₄:Eu, Nd" synthesized via an oxalate co-precipitation method as a function of the heating temperature. In Fig. 1, the characteristic peaks of the SrAl₂O₄ phase with a single phase monoclinic structure was observed at 800 °C. The crystallinity of the SrAl₂O₄ powders increased on increasing the heating temperature. The crystallization of the SrAl₂O₄ phase was completed at 1200 °C. The XRD patterns in Fig. 2 indicate that the "CaAl₂O₄:Eu, Nd" phosphor prepared through an oxalate coprecipitation method



Fig. 1. XRD patterns of "SrAl₂O₄:Eu, Dy" synthesized by an oxalate co-precipitation method.

(net) (net) (a) 1300 °C (b) 1300 °C (c) 1200 °C (c)

Fig. 2. XRD patterns of "CaAl₂O₄:Eu, Nd" synthesized by an oxalate co-precipitation method.



Fig. 3. Microstructure of (a) "SrAl₂O₄:Eu, Dy" and (b) "CaAl₂O₄: Eu, Nd" by an oxalate co-precipitation method.

could be crystallized at 1000 °C. The microstructural morphologies of the phosphor powders prepared by an oxalate coprecipitation method are shown in Fig. 3.



Fig. 4. Photoluminescence spectra of "SrAl₂O₄:Eu, Dy" synthesized by oxalate co-precipitation method.

The phosphorescent phosphors, which were obtained through an oxalate coprecipitation method, showed a smaller particle size compared to the powders fabricated by a solid-state method.

The photoluminescence spectrum of the SrAl₂O₄:Eu, Dy phosphor synthesized by an oxalate coprecipitation method are shown at the wavelength of 514 nm (Fig. 4), which is due to the substitutional defect of the Eu^{2+} , Dy³⁺ ion to the Sr or Al site in the crystal defect level of the SrAl₂O₄:Eu, Dy. Because the photoluminescence spectrum of the phosphor with the Dy³⁺ activator ion was not detected near 580 nm, the luminescent center of the SrAl₂O₄:Eu, Dy phosphorescent phosphor can be interpreted to originate from the contribution of the Eu^{2+} activator ion [11]. Also, the photoluminescence spectrum of the SrAl₂O₄:Eu, Dy phosphor, detected at a wavelength of 514 nm, can be explained as a $4f^{6}5d-4f^{7}$ transition in the Eu^{2+} activator ion [13]. Thus, it was found that the excitation wavelength of 254 nm and 365nm induced the luminescent spectrum near 520 nm through the $4f^{6}5d \rightarrow 4f^{7}$ transition in the Eu²⁺ ion for the SrAl₂O₄:Eu, Dy phosphor. The color coordinates of the SrAl₂O₄:Eu, Dy phosphor, obtained by fluorophotometer analysis, showed the color coordinates (x, y) of 0.3442, 0.5203.

The photoluminescent spectrum of the CaAl₂O₄:Eu, Nd phosphor is shown at the peak wavelength of 476 nm at the excitation wavelengths of 245 nm and 365 nm (Fig. 5), which originates from the 5d-4f transition according to the substitution of the Eu²⁺ ion on the Ca²⁺ ion site. It appears that the luminescent spectrum in a wide wavelength range of the CaAl₂O₄:Eu, Nd phosphor is based on the interaction of the matrix and the activator ion. It is considered that the major luminescent spectrum by the 5d-4f transition in the Eu²⁺ ion is rarely influenced by introduction of the Nd²⁺ activator ion into the matrix. The CaAl₂O₄:Eu, Nd phosphor showed the color coordinates (x, y) of 0.1853, 0.3969 as a blue phosphor.



Fig. 5. Photoluminescence spectra of "CaAl₂O₄:Eu, Nd" synthesized by an oxalate co-precipitation method.

Conclusions

The "SrAl₂O₄:Eu, Dy" and "CaAl₂O₄:Eu, Nd", longphosphorescent phosphors were synthesized from metal oxalate precursors using an aqueous solution and oxalic acid and heated at 1000 °C, and then annealed under a reducing atmosphere of mixed gases of 5% H_2/N_2 . The crystallization behavior of the phosphors at a relatively low temperature could be achieved through a homogeneous mixing of the starting materials in the aqueous solution. The emission spectrum near 514 nm of the SrAl₂O₄:Eu, Dy phosphor, synthesized by an oxalate coprecipitation method, was observed with excitation wavelengths of 254 nm, 365 nm through the $4f^{6}5d \rightarrow$ $4f^7$ transition of the Eu²⁺ ion. On the other hand, the emission spectrum of the CaAl₂O₄:Eu, Nd phosphor was at a wavelength of 476 nm through the 5d-4f transition of the Eu^{2+} ion.

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