Effects of Sintering Temperature on Ce$^{3+}$-doped Ca$_3$Y$_2$Si$_3$O$_{12}$ Blue-emitting Oxide Phosphors

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Blue phosphors of Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$ have been synthesized by using a facile solid-state reaction method at various sintering temperatures from 1300 to 1600 °C in a reducing carbon atmosphere. The Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$ samples were crystallized into an orthorhombic phase, and the intensity of the main (230) peak depended on the sintering temperature. The particle size of the samples increased gradually with increasing sintering temperature. Field-emission scanning electron microscopic images confirmed that the particles acquired irregular shapes. Using a fluorescence spectrophotometer, we investigated the photoluminescent properties by excitation (348 nm) and emission (421 nm, 5d$^1 \rightarrow 2F_{7/2}^0$ and $2F_{5/2}^0$) spectra. The intensity of the photoluminescence spectrum was the highest when the sample was sintered at 1600 °C. The calculated CIE coordinates were found to be (0.165, 0.127), which are located in the blue region.

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I. INTRODUCTION

Recently, phosphors with high performance, for example, thermal and chemical stability, including broad band emission with suitable morphology, have attracted much attention for their applications in different devices, such as field emission displays (FEDs), high-resolution, florescence lamp, back lighting for liquid crystal TV, high-power headlights, phosphor-converted white-light-emitting diodes (PC-LEDs), and white LEDs [1–4]. Particularly, white LEDs are produced by using a blue LED and a yellow emitting phosphor. However, this process suffers from a low color-rendering index due to the mixing of two colors [2]. An RGB phosphor converted UV LED can be an alternative solution to overcome this problem of the white LED. Therefore, we try to make better blue phosphor materials.

In phosphors, rare-earth ions act as activators or sensitizers. Activators absorb the energy from the host lattice and re-emit it as light, and sensitizers deliver the energy to activators via the host lattice, and then the activators emit light. The important thing is the choice of activators, hosts and synthesis methods because the emission wavelength and intensity are changed by activators, hosts, and synthesis methods. Many methods are used to synthesize phosphors, such as the solid-state reaction [5], co-precipitation [6], solvothermal [3], and sol-gel [7] methods. Among them, the solid-state reaction has various advantages such as low expenses and suitability for mass production.

Ca$_3$Y$_2$Si$_3$O$_{12}$ was first described and its structural properties reported in 1997 by Yamane et al. [8]. Chiu et al. reported on the Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$, Tb$^{3+}$ [9], luminescence of Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$, Mn$^{2+}$ [10]. In particular, data relative to the promising host Ca$_3$Y$_2$Si$_3$O$_{12}$ show that it is transparent in the UV region [11], and rare-earth ions doped in silicate-based hosts have been gaining much interest from researchers owing to their improved optical properties [12–14]. The cerium ion is the most important activator for blue emission from different phosphor host lattices [15]. The spectra of the 5d energy levels are well known to depend on the Stokes shift and the crystal field splitting [16].

In this research, Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$ phosphors were
The lifetimes of the powders were measured by using a fluorimeter with a Xe arc-lamp at a power of 60 W. The size and the shape of the particles, the photoluminescence (PL) and the PL excitation (PLE) were investigated by using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and fluorescence spectrometry.

II. EXPERIMENTS

From the initial materials CaCO$_3$ (99.5%, Aldrich), Y$_2$O$_3$ (99%, Aldrich), SiO$_2$ (99.99%, Aldrich) and CeO$_2$ (99.99%, Aldrich, 0.03 mol), Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$ phosphor powders were synthesized by using a solid-state reaction. According to the chemical equation, the mixing of various constituents was carried out by using a planetary ball mill (350 rpm, 10 h) with zirconia balls while adding a small amount of acetone. After the mixed samples had been dried at 70 °C for 24 h, they were finely ground in an alumina mortar. The obtained mixtures were sintered in a reducing carbon atmosphere at temperatures of 1300, 1400, 1500, and 1600 °C for 4 h.

Thermogravimetric/differential thermal analyses (TG/DTA) of the Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$ phosphor were carried out with a Material Analysis and Characterization TG-DTA 2000 system. This experiment was carried out at a heating rate of 10 °C/min, and the samples were heated from room temperature to 1200 °C. The XRD data were collected in the range of 10 − 70° at a scan speed 2°/min by using a Philips, X’Pert-MPD X-ray diffractometer with a 3-kW Cu-K radiation ($\lambda = 0.154056$ A) X-ray tube. The surface morphology of the powders was examined by using FE-SEM (JSM-6700, JEOL). The room-temperature photoluminescence (PL) spectra of the Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$ phosphors were recorded on a PTI (Photon Technology International) fluorimeter with a Xe arc-lamp at a power of 60 W. The lifetimes of the powders were measured by using a phosphorimeter attachment to the main system with a Xe flash lamp (25-W power).

III. RESULTS

The TG-DTA curves of the Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$ phosphor in an air atmosphere are shown in Fig. 1. Two different steps of weight loss were observed from the thermogravimetric (TG) curve: one in the temperature range of 140 − 300 °C and the other in the temperature range of 700 − 800 °C. The first TG region corresponds to the evaporation of water from the surfaces of the phosphor particles. In the second TG region, the loss weight is sharply decreased because it corresponds to the decomposition of organic species such as CO$_2$ from the CaCO$_3$ group. Four endothermic DTA peaks, one each at 194, 730, 808, and 1025 °C, were found to be related to the TG curve. The endothermic peak at 194 °C is caused by the evaporation of water, and the peaks at 730 and 808 °C are caused by the evaporation of CO$_2$.[17] The last endothermic peak at 1025 °C is due to the formation of the crystal structure; therefore, the slope of the TG curve gradually becomes stabilized at temperatures above 1000 °C.

The XRD patterns of Ca$_3$Y$_2$Si$_3$O$_{12}$:Ce$^{3+}$ phosphors at different sintering temperatures are shown in Fig. 2. The structure of the samples is observed to be orthorhombic (Pnma space group), and the lattice parameters are $a = 6.536$ nm, $b = 15.62$ nm, and $c = 10.029$ nm, corresponding to the JCPDS card No. 87-0453. Ca$_3$Y$_2$Si$_3$O$_{12}$ is like an isotypic ternesite, Ca$_3$(PO$_4$)$_2$(SiO$_4$). The formula is similar to that of a garnet, A$_3$B$_2$(SiO$_4$)$_3$, and the blended occupation of A and B sites by Ca$^{2+}$ and Y$^{3+}$ leads to disorder. As a result, the structure of Ca$_3$Y$_2$Si$_3$O$_{12}$ can be expressed as AB$_2$C$_2$(SiO$_4$)$_3$. A, B and C corresponds