Original Research Paper

Low temperature synthesis of YAG:Ce^{3+} phosphor by mechanical method

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ABSTRACT

Here, we report on the effect of mixing state of raw materials on the solid-state synthesis of Ce^{3+}-doped Y$_3$Al$_5$O$_{12}$ (Y$_{2.97}$Al$_5$O$_{12}$:Ce$_{0.03}^{3+}$, YAG:Ce^{3+}) phosphors for white light emitting diodes. The mixed powders were prepared by the mechanical method using an attrition-type mill. Homogeneously mixed powder in nanoscale of raw powder materials was favorably obtained by the mechanical method. It achieved the synthesis of YAG:Ce^{3+} by heating at 1400 °C which was 400 °C lower than the synthesis temperature of the mixed powder by ball milling. Besides, larger crystallite size was obtained by heating the powder at higher temperature. The YAG:Ce^{3+} phosphor synthesized at 1800 °C exhibited the largest crystallite size, thus led to maximum external quantum yield of 55%, and the luminous efficiency of 97% at 150 °C. It revealed the highest efficiency in the previously reported values.

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1. Introduction

Ce^{3+}-doped Y$_3$Al$_5$O$_{12}$ (yttrium aluminum garnet, YAG) phosphors have been widely used for white light emitting diodes (LEDs). A blue LED excitation of Ce^{3+} leads to the yellow 5d → 4f emission band. The complementary relationship between blue and yellow gives white light. The emission wavelength can be easily controlled by changing the chemical composition of host materials [1,2]. Furthermore, the manufacture of YAG:Ce^{3+} phosphor is low cost compared with other phosphors. Conventionally, YAG:Ce^{3+} phosphor is manufactured by solid-state reaction at high temperatures. The raw powders such as Y$_2$O$_3$, Al$_2$O$_3$, and CeO$_2$ are mixed by ball milling under dry or wet conditions, and then the mixed powder is calcined for a few hours over 1600 °C to obtain YAG:Ce^{3+} [3]. On the other hand, a decrease of the calcination temperature is necessary from a view point of energy saving. To decrease the synthetic temperature, the addition of BaF$_2$ as a flux has been reported [4]. A single phase YAG:Ce^{3+} was obtained at lower temperature. BaF$_2$ reacts with raw materials to form eutectic compositions with lower melting point, and the subsequent solid–liquid reaction proceeds to the formation of YAG:Ce^{3+}. However, the flux method still needs much energy by the complicated process including washing of the product by acid, and needs additional cost of flux.

The emission intensity of YAG:Ce^{3+} phosphor is improved by the particle growth [4,5]. In addition, the properties of thermal quenching of YAG:Ce^{3+} phosphor are related to the thermal relaxation from a 5d excited state to a 4f ground state [6,7], and greatly affected by the band gap and the defect of its host material [8]. To obtain the high-quality YAG:Ce^{3+} phosphor with a single phase and larger crystallite size by solid-state synthesis, the preparation of the homogeneous mixed powder of raw materials in nano-scale is required, thus leads to lower temperature synthesis and larger crystallite size by further heating [9,10]. However, the relationship between the mixing state of the starting powder and the fluorescence properties of the synthesized phosphor remains to be unclear.

The particle size and the mixing state of raw materials are important for lowering the synthetic temperature of YAG:Ce^{3+} and gaining its high-quality phosphor. In this paper, we focused on the mixing state of nano-sized raw materials for the solid-state synthesis of the YAG:Ce^{3+} phosphor. The raw materials of YAG:Ce^{3+} were processed by using an attrition-type mill, and the mixed powders were calcined at various temperatures. The fluorescent properties of the obtained YAG:Ce^{3+} phosphors were evaluated.

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2. Experimental

2.1. Raw materials

Nano-sized powders of Y_2O_3, Al_2O_3, and CeO_2 were used as raw materials. These high-purity powders were purchased from Kojundo Chemical Laboratory (Japan). Some characteristics of these powders are summarized in Table 1. The median size (D_{50}) of the raw powder was calculated by the particle size distribution, measured by the laser diffraction-scattering method (Microtrac MT3300EXII, NIKKISO, Japan). The specific surface area (S_w) of raw powders was measured by a N_2 adsorption instrument (micromeritics ASAP2010, Shimadzu, Japan) based on the BET method. The primary particle size (d_{BET}) was calculated from the BET specific surface area as follows: $d_{BET} = 6/(\rho \cdot S_w)$, where ρ is a theoretical density. The primary particle sizes of the used Y_2O_3, Al_2O_3, and CeO_2 were 72 nm, 134 nm, and 5 nm, respectively.

2.2. Powder mixing and solid-state reaction

In this study, we selected the chemical composition of $Y_{2.97}Al_5O_{12}:Ce_{0.03}^{3+}$ as YAG:Ce^{3+}. Stoichiometric quantities of raw materials (total amount of 30 g) were put into the chamber of an attrition-type mill. The milling apparatus has been illustrated elsewhere [11]. The main parts of this mill are a fixed chamber (inner diameter of 80 mm, depth of 50 mm) and an oval rotor, which made by a stainless steel. The gap between the chamber and the rotor was fixed at 1 mm. The powder processing by using this attrition-type mill was carried out while cooling the chamber wall by water. The milling was conducted at electric power of 2 kW for 5 min and 3 kW for 30 min, where this electric power is defined as the load power applied to the motor shaft. For the sake of simplicity, the mixed powders obtained at 2 kW for 5 min and at 3 kW for 30 min are denoted as sample A and sample B, respectively. In order to compare the mixing state of raw materials, the conventional ball mill was also conducted. The same amounts of raw materials were put into a ZrO_2 pot together with ZrO_2 balls (diameter of 5 mm). The ball milling was performed at a rotation speed of 60 rpm for 6 h. The ball milled powder is denoted as sample C.

YAG:Ce^{3+} phosphors were synthesized by solid-state reaction. The mixed samples A, B, and C were calcined from 1200 °C to 1800 °C for 3 h in a N_2 atmosphere. After synthesis, the YAG:Ce^{3+} products were pulverized to get powders.

2.3. Characterization

The particle morphology was observed by scanning electron microscopy (SEM, Carlzeiss, Ultra plus). The crystalline phases of the YAG:Ce^{3+} products were identified by a powder X-ray diffraction measurement system (XRD, Rigaku, Ultima IV). The crystallite size (D) was estimated from the Scherrer equation as follows: $D = 0.9\lambda/(\beta \cdot \cos\theta)$, where λ is the employed X-ray wavelength, θ is the diffraction angle, and β is defined as the half-width. Crystallite size was estimated by using (400) peak of YAG phase.

The photoluminescence (PL) properties were measured by a fluorescence spectrophotometer (HITACHI, F-7000). The external quantum yield (QY_o) and the temperature quenching were measured by a quantum yield measurement device (Hamamatsu Photonics Quantaurus-QY C11347-01).

3. Results and discussion

3.1. Mixing state of raw materials

Table 2 shows the powder properties of the mixed powders. By the strong compressing and shearing forces, the median size (D_{50}) and primary particle size (d_{BET}) of the mixed samples of A and B were larger than those of the mixed sample C. However, their particle size d_{BET} ranged less than 200 nm. Figs. 1 and 2 show the SEM images and EDX elemental maps of the mixed powders obtained by the mechanical milling and the ball milling.

Table 2
Powder properties of the mixed powders prepared under different mixing conditions.

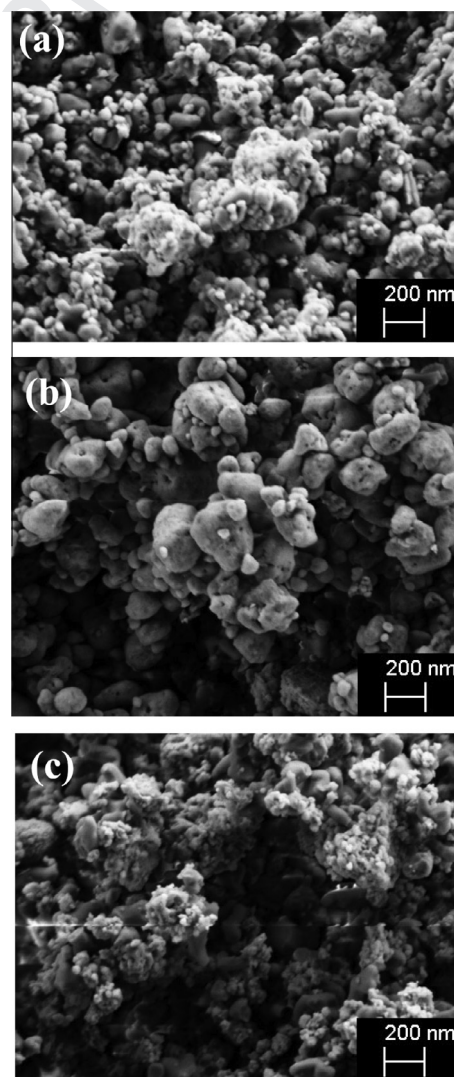| Sample	Mixing condition	D_{50} (μm)	S_w (m²/g)	d_{BET} (nm)
A	2 kW–5 min	0.6	13.4	88
B	3 kW–30 min	0.8	6.9	171
C	Ball milling-6 h	0.5	16.2	73

Fig. 1. SEM images of the mixed powders: (a) sample A (attrition type mill, 2 kW, 5 min), (b) sample B (attrition-type mill, 3 kW, 30 min), and (c) sample C (ball mill, 6 h).

Table 1
Powder properties of the starting materials used in this study.

Materials	Purity (%)	D_{50} (μm)	S_w (m²/g)	d_{BET} (nm)
Y_2O_3	99.99	0.6	17.2	72
Al_2O_3	99.99	0.4	11.3	134
CeO_2	99.99	0.3	163.4	5