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Combustion synthesis of YAG:Ce phosphors via the thermite reaction of aluminum

Junpei Ohyama [a], Chunyu Zhu [b, c], Genki Saito [a, *], Miki Haga [a], Takahiro Nomura [a], Norihito Sakaguchi [a], Tomohiro Akiyama [a]

[a] Center for Advanced Research of Energy and Materials, Hokkaido University, Kita 13 Nishi 8, Kitaku, Sapporo 060-8628, Japan
[b] Division of Applied Chemistry & Frontier Chemistry Center, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
[c] Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

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ABSTRACT

Cerium-doped yttrium aluminum garnet (YAG:Ce) as a yellow phosphor for white light-emitting diodes (LEDs) was synthesized via a facile combustion method using Y_2O_3, CeO_2, Al_2O_3, Al, and $NaClO_4$ as raw materials. The combustion synthesis approach utilizes the strong exothermic oxidation of aluminum to realize a self-sustaining reaction. In this study, we investigated the effects of the ratios of Al_2O_3 to Al, fluxes, and coprecipitated materials as raw materials on the luminescence properties of the synthesized YAG:Ce phosphors. When the amount of Al_2O_3 x is varied, the combustion reaction proceeds at $x \leq 1.8$, with $x = 1.725$ being the optimum condition for producing a high-performance product. When 5 wt% BaF_2 is added, the luminescence intensity is significantly improved owing to a decrease of YAP ($YAlO_3$) formation with improved uniformity. However, the addition of CaF_2 and NaF does not improve the luminescence properties. To suppress the segregation of CeO_2, we used the coprecipitated material Y_2O_3 $-CeO_2$ as a raw material. Unlike with separate addition of Y_2O_3 and CeO_2, Ce ions are uniformly distributed in the coprecipitated material, resulting in improved luminescence properties. The combination of BaF_2 and coprecipitated material significantly improves the internal quantum efficiency to 83.0%, which is close to that of commercial phosphors.

1. Introduction

Ce-doped $Y_3Al_5O_{12}$ (YAG:Ce) phosphors have been widely used as yellow phosphors for white light-emitting diodes (LEDs) owing to their high emission efficiency under blue light excitation. In conventional solid-state reactions, the synthesis of pure YAG:Ce phosphors requires high-temperature (>1500 °C) treatment, which is both energy- and time-consuming. Therefore, lower temperature syntheses, such as spray pyrolysis,[1] sol–gel processing,[2–4] coprecipitation method,[5,6] citrate sol–gel combustion preparation,[7–10] and hydrothermal synthesis,[11] have been proposed. However, these processes require the use of nitrates, such as $Al(NO_3)_3$ and $Y(NO_3)_3$, which still necessitate the use of high temperature treatments. To resolve this problem, this paper proposes a combustion synthesis (self-propagation high-temperature synthesis) of YAG:Ce phosphor using aluminum oxidation heat. Combustion synthesis using the thermite reaction of Al employs the propagation of a strong exothermic reaction, namely, Al oxidation, which is a self-sustaining reaction. This method has advantages of low energy consumption and short reaction times, and has been applied to produce a variety of advanced materials, such as oxides,[12–14] nitride/oxynitride ceramics,[15–17] and intermetallics.[18,19]

In this study, we examined the facile and effective combustion synthesis of YAG:Ce phosphors via the thermite reaction of Al, where the oxidation heat of Al is used for self-propagation of the high-temperature synthesis. The key for successful combustion synthesis of YAG:Ce phosphors is regulating the reaction temperature, which can be optimized by controlling the ratio of Al and Al_2O_3 in the raw materials. We also investigated the effects of fluxes and coprecipitated materials on the luminescence properties of the synthesized YAG:Ce phosphors. It is known that flux addition greatly influences ion diffusion and crystallization processes, resulting in improved phase uniformity and luminescence properties.[1,20] For single crystalline YAG growth, fluxes such as $PbO–PbF_2$ and $PbO–PbF_2–B_2O_3$ have been used.[21] Among the various available fluxes, fluoride-type fluxes such as BaF_2, CaF_2, MgF_2, and AlF_3 have been found to be effective for aluminate-type phosphors.[20,22,23] However, the effect of these fluxes on combustion-synthesized

* Corresponding author.
E-mail address: genki@eng.hokudai.ac.jp (G. Saito).

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phosphors is unknown. In addition, we studied the effect of utilizing coprecipitated Y_2O_3–CeO_2 as a raw material. Because Y and Ce ions are uniformly distributed in the coprecipitated material, suppression of CeO_2 segregation and increased uniformity are expected.

2. Material and methods

YAG:Ce phosphors with a Ce ratio of 1.0 at% were prepared from commercially available Y_2O_3 (99.99% purity), CeO_2 (99.99% purity), Al_2O_3 (99.99% purity), Al (99.99% purity), and $NaClO_4$ (98% purity) powders. Al_2O_3 acts as a diluent to control the combustion flame temperature. The reaction formula for the combustion synthesis can be written as shown in Eq. 1.

$$1.485Y_2O_3 + 0.03CeO_2 + xAl_2O_3 + (5-2x)Al + yNaClO_4 \rightarrow Y_3Al_5O_{12} + yNaCl;\ (y = (7.485-3x)/4) \quad (1)$$

Here, x refers to the amount of Al_2O_3. The adiabatic flame temperature decreases with the increase of x. First, seven sets of raw materials were prepared by balancing the molar ratios with x ranging from 1.5 to 1.9. BaF_2 (99.9% purity), NaF (≥99.9% purity), and CaF_2 (99.9% purity) were used as fluxes, at ratios of 0–7 wt%, 0–5 wt%, and 0–5 wt%, respectively. Y_2O_3–CeO_2 as a coprecipitated material with a Ce concentration of 5 at% (Nippon Yttrium Co., Ltd.) was also used as raw material.

The raw powders were mixed well in a rolling ball mill at a rate of 100 r/min for 4 h. The mixed raw powders were then placed in graphite crucibles (120 mm × 40 mm × 40 mm), which were ignited and combusted in an Ar-filled reactor, as shown in Fig. 1. The main components of the reactor are a stainless steel chamber, a control unit, and a gas control system. Before ignition, the reactor was evacuated using a rotary pump, and Ar gas was supplied to maintain atmospheric pressure. A disposable carbon foil was placed in contact with one end of the reactant, which was then electrically ignited using a voltage of 50 V and a current of 100 A at room temperature. After ignition, the exhaust valve was opened for 15 min until the product cooled down. The collected products were crushed and washed with distilled water to remove any soluble impurities (mainly NaCl).

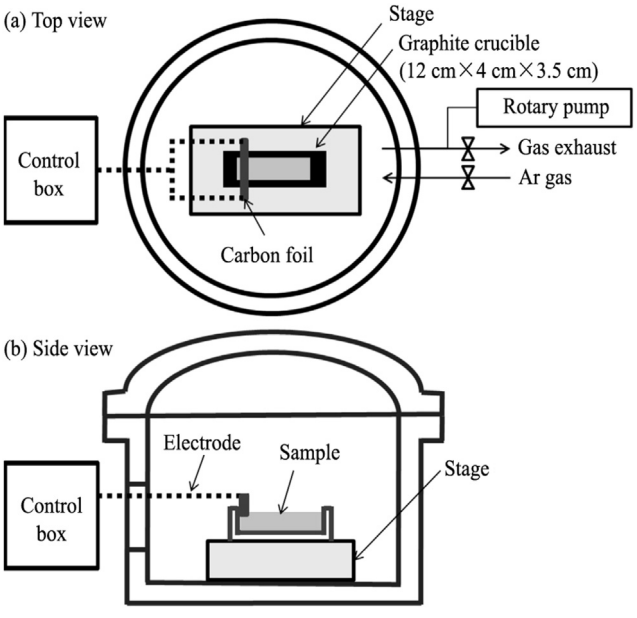

Fig. 1. Schematic diagram of the experimental apparatus for preparing samples by combustion synthesis.

The product phases were analyzed using X-ray diffraction (XRD, Miniflex600, Rigaku) with Cu Kα radiation (λ = 1.54056 nm). The photoluminescence properties were recorded using a spectrofluorometer (FP-6200, JASCO) at room temperature with an excitation wavelength of 460 nm. The internal quantum efficiency was quantitatively determined using a fluorescence spectrometer (FP-8500, JASCO) equipped with an integrating sphere (ISF + 834, JASCO). For cross-sectional elemental analysis of the particles, the obtained particles of 0.1 g were mixed with 2 g fine copper powder, and then hot pressed for 1 h at 250 °C to form a bulk sample, which was cut, polished, and ion milled using a cross-section polisher (IB-09010CP, JEOL). SEM-EDS (JSM-7001FA, JEOL) was used to confirm the elemental distribution. The valance of Ce ions in the synthesized phosphor was analyzed using XPS (JPS-9200, JEOL).

3. Results and discussion

3.1. Effect of Al_2O_3 ratio in raw materials

In this work, the combustion synthesis of YAG:Ce was promoted by the oxidation of Al by O_2, which was released from $NaClO_4$. The reaction temperature for the oxidation of Al can be in excess of 5300 °C, which can cause melting and extreme sintering of the products. Therefore, we added Al_2O_3 as a diluent, and studied the optimum amount x of Al_2O_3. Fig. 2 shows photographs of samples obtained by combustion synthesis at different x values, as indicated in Eq. 1. The raw materials were in the form of gray powders. The combustion synthesis afforded yellow porous bulk materials with precipitated white powders of NaCl. The raw materials were ignited from one end of the crucible. For samples with x = 1.5–1.8, yellow products were obtained throughout the crucible, which indicates that the raw materials were successfully ignited and the combustion reaction was propagated. However, excluding the ignition area, which showed a color change to yellow, the sample at x = 1.9 appeared the same as the raw material, indicating that combustion propagation failed owing to an excess amount of Al_2O_3 as a diluent. For samples with x = 1.5–1.6, the obtained yellow product seemed to be considerably melted, and a large amount of dark sintered agglomerates was obtained, which might be caused by a very high reaction temperature at higher Al ratios. For samples with x = 1.75–1.8, gray powders remained on the surface of the products, especially for samples with higher x values, indicating unreacted materials. In contrast, the products obtained at x = 1.7–1.725 showed the cleanest yellow color, suggesting the best conditions for producing YAG:Ce.

Fig. 3 shows XRD patterns of the products obtained at x = 1.5–1.9. For x = 1.5 and 1.6, the dark sintered agglomerates were removed from the XRD samples owing to difficulties in crushing these materials. The white product collected from the wall of the crucible and

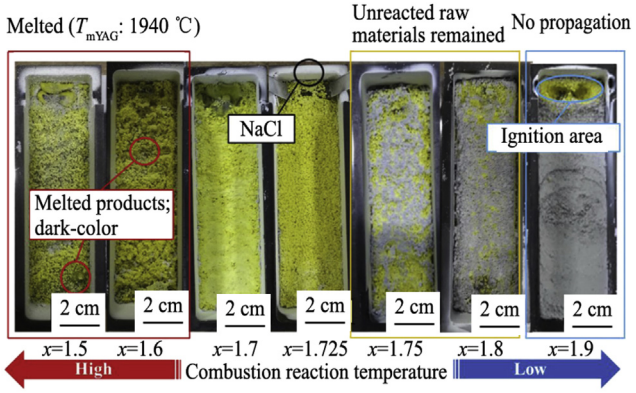

Fig. 2. Photographs of products after combustion synthesis at different x values.