

Comparison of YAG : Eu phosphors synthesized by supercritical water in batch and continuous reactors

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Abstract—Luminescent yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) nanoparticles doped with Eu (10 at%) were synthesized in batch-type and continuous-type supercritical water (SCW) reactors. In the case of the continuous-type SCW method, the particles of YAG : Eu phosphors were much smaller and demonstrated a uniform spherical-like shape. Inversely, in the case of the batch-type SCW method, a needle-like or elliptical-like shape was formed because a finite amount of time was required to reach SCW conditions from ambient conditions. However, the emission intensity of YAG : Eu phosphors synthesized by using the batch-type SCW method was stronger. Therefore, it is concluded that the continuous-type SCW method is superior to the batch-type SCW method from the viewpoint of the particle size and shape, but the luminescence property of phosphors in the continuous-type SCW method needs to be improved. In addition, a calcination process slightly improved the luminescence intensities of YAG : Eu phosphors generated by using either the batch-type or continuous-type SCW methods.

Key words: Supercritical Water, $Y_3Al_5O_{12}$ (YAG), Luminescent Properties, Batch Reactor, Continuous Reactor, Nanoparticle Phosphors

INTRODUCTION

In recent years, inorganic phosphors have been studied extensively for applications in various types of display panels, such as the plasma display panel (PDP), the vacuum fluorescent display (VFD) and the field emission display (FED) [1]. In order to improve the brightness and resolution of these displays, much effort has been expended to develop phosphors having high quantum efficiency, controlled morphology, and fine particle sizes.

Due to the excellent chemical, physical, and optical properties of yttrium aluminum garnet (YAG), YAG-based phosphors have been widely used in the preparation of displays [2]. YAG phosphors are generally synthesized at high temperatures for an extended period of time by a solid-state reaction process. However, the solid-state reaction usually produces several by-products such as $Y_4Al_2O_9$ (YAM) and $YAlO_3$ (YAP) due to insufficient mixing and low reactivity of raw materials. In addition, phosphor particles synthesized from conventional solid-state reactions have relatively large sizes [3].

In order to solve these problems, various methods have been developed to synthesize the YAG phosphors, including hydrothermal synthesis [4], a sol-gel method [5,6], spray-pyrolysis synthesis [7,8], combustion processes [9,10], and a hydroxide co-precipitation method [11]. Recently, supercritical water (SCW) has gained considerable attention as an excellent medium for the synthesis of functional inorganic materials. The static dielectric constant of SCW is similar to that of non-polar solvents (<2) even though that of water at ambient conditions is about 80 [12]. Hence, near the critical point of water, the rate of hydration of metal salts increases due to the

decrease of the dielectric constant, but the solubility of the metal oxide decreases rapidly [13,14].

Utilizing the unique characteristics of SCW, the phosphors can be synthesized by batch-type or continuous-type methods. Although the media in which the process is conducted is the same in both methods, the operating methods are significantly different from each other. Therefore, the need exists for products synthesized by each method under the same or similar conditions to be compared to each other.

In this study, YAG : Eu phosphor particles were synthesized by using batch-type and continuous-type SCW methods. The particle size, shape, crystallinity, and photoluminescence characteristics of YAG : Eu particles synthesized by both SCW methods were compared to each other by using x-ray diffraction (XRD) patterns, scanning electron microscopic (SEM) images, and photoluminescence spectra.

EXPERIMENTAL

1. Materials

In this study, three types of metal nitrates were used as precursors: yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$, Strem Chemicals, 99.9%), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Wako Chemicals, 99.9%) and europium nitrate hexahydrate ($Eu(NO_3)_3 \cdot 6H_2O$, Strem Chemicals, 99.9%). The three nitrates were dissolved together in deionized water. Thereby, a solution having the general formula, $(Y_{1-x}Eu_x)_3Al_5O_{12}$ at $x=0.1$, was obtained. Subsequently, the pH value of the solution was adjusted to a value of approximately 7, 9, or 11 with KOH (Aldrich Chemicals, 99.99%).

2. Synthesis of YAG : Eu in a Batch Reactor

YAG : Eu was synthesized at 300 bar and 400 °C in a batch-type SCW reactor without mixing. The concentrations of yttrium nitrate and aluminum nitrate were 0.015 M and 0.25 M, respectively. The

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suspension in the batch reactor was heated to 400 °C and held at that temperature for 2 h. During the reaction period, the pressure gradually increased to 300 bar. When the reaction was completed, the reactor was cooled to room temperature. Particles were recovered from the resulting suspension by suction filtration and were dried in an oven at 105 °C for 24 h. The detailed procedures and description of the apparatus can be found in the literature [15].

3. Synthesis of YAG : Eu in a Continuous Reactor

YAG : Eu was synthesized at 280 bar and 400 °C in a continuous SCW reactor. Because the control of pressure and temperature was difficult for this system, the pressure applied to the continuous SCW system was lower than the pressure applied to the batch SCW system.

Initially, deionized water was introduced through all the inlet lines. After reaching steady-state pressure and temperature, the aqueous metal salt solution, the KOH solution and deionized water were fed into the reactor.

The feed was preheated to maintain SCW conditions at the upper portion of the reactor. The high-temperature-mixed solution was then fed into the reactor which was filled with SCW. The phosphors in the continuous reactor synthesized at 20 sec residence time in this study. After cooling of the effluent solution, particles were obtained by filtration and were dried in an oven at 105 °C for 24 h. Detailed information concerning the apparatus and procedures was reported in a previous study [16].

4. Characterization

The crystalline properties of the particles were determined with an X-ray diffractometer (Rigaku model D/max-3A). The size and morphology of the particles were analyzed by using SEM (Hitachi Corp., S-4200). Luminescence spectra were measured with a luminescence spectrometer (Perkin-Elmer LS50-B) under ultraviolet (UV) light with a Xe flash lamp.

RESULTS AND DISCUSSION

The luminescent properties of phosphors are influenced by the pH value of the initial solution. When emission spectra were acquired for YAG : Eu phosphors that were synthesized under various pH conditions (approximately pH 7, 9, and 11), it was determined that as the pH increased, the emission intensity of the YAG : Eu³⁺ nanoparticles was increased by using both batch-type [15] and continuous-type [16] SCW methods. However, the YAG : Eu³⁺ nanoparticles synthesized at approximately pH 9 in both continuous and batch reactors showed the highest luminescent intensities, although all of the particles synthesized under various pH conditions were pure YAG nanoparticles.

In this study, the phosphors synthesized by using batch-type and continuous-type SCW methods were compared at approximately pH 9, the condition which demonstrated the highest luminescent intensities. That is, the YAG : Eu phosphor synthesized at pH 9.41 by using the batch-type method was compared to that prepared at pH 9.10 by the continuous-type method. For a clear comparison, the Eu concentration was fixed at 10 atomic % (at%) in both methods and the reaction time in the continuous-type method was set at 20 s. Since the pressure in the batch system was affected by the system temperature, it was not easy to make the pressure the same as that in the continuous system. In addition, it was hard to make the same

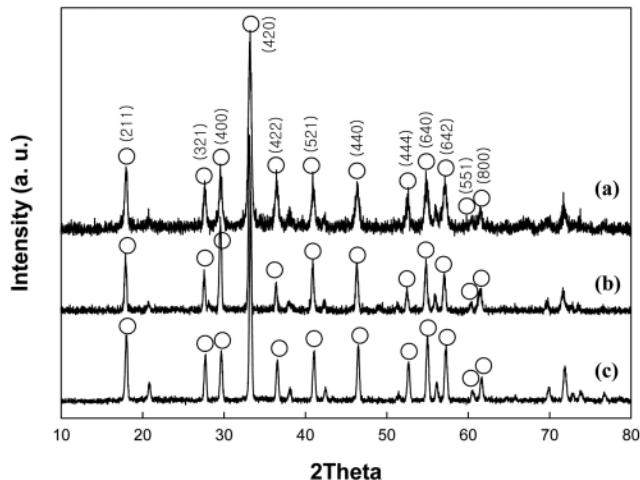


Fig. 1. XRD patterns of YAG : Eu phosphors synthesized by SCW processes: (a) continuous-type SCW (Eu conc.: 10 at%, reaction time: 20 s, pH: 9.10), (b) batch-type SCW (Eu conc.: 10 at%, pH: 9.41), (c) standard YAG peak.

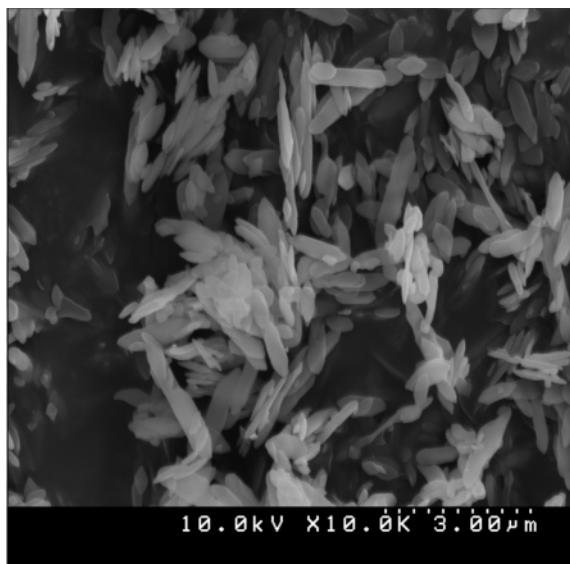
pH condition in the continuous system because the solution was continuously supplied with reactants and water. Therefore, slightly more favorable conditions, higher pressure and pH, were applied to the batch system.

In Fig. 1, the XRD patterns of YAG : Eu phosphors synthesized in batch and continuous SCW reactors were compared to the standard YAG peak. As a result, both XRD peaks of the synthesized phosphors were virtually coincident with the pure YAG standard peak. It has been reported that the existence of by-products was previously observed in various synthetic methods for YAG nanoparticles prior to further treatment [17]. In this research, regardless of applying batch-type or continuous-type methods, however, no by-product peaks such as YAM or YAP were observed (Fig. 1). Therefore, pure crystalline YAG can be successfully obtained by using SCW regardless of whether batch-type or continuous-type methods are used for synthesis.

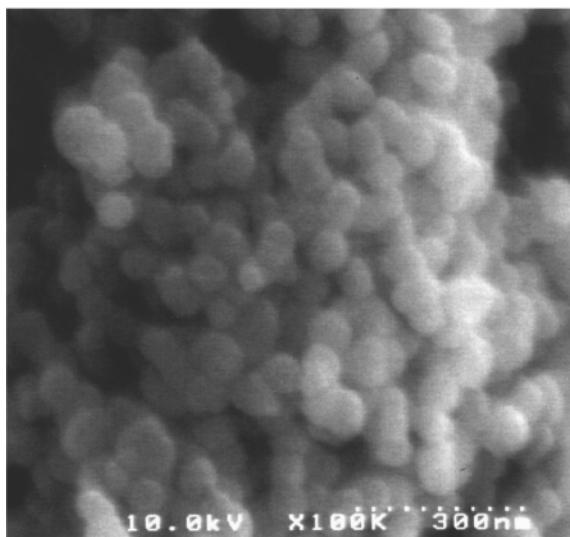
Size and shape are also important characteristics of the particles influencing the luminescent properties of phosphors. Previously, it was reported that phosphor materials should have a fine (<3 μm) and narrow size distribution in order to display strong luminescent properties [18].

In Fig. 2, SEM images of YAG : Eu phosphors prepared from batch-type and continuous-type SCW methods are compared. The particle size of YAG : Eu synthesized by the batch-type SCW method was in the range of 0.5-3 μm. Conversely, the particle size of YAG : Eu prepared by using the continuous-type SCW method was approximately 60 nm. Much smaller YAG : Eu phosphors were synthesized from the continuous-type SCW method than from the batch-type SCW method. Moreover, the particle sizes of YAG : Eu phosphors prepared by the batch-type SCW method were even smaller than the particle sizes produced by using a solid-state reaction process (5-10 μm [19]).

The shape of YAG : Eu phosphors from the batch-type SCW method appears to be needle-like or elliptical-like (Fig. 2a), while particles generated from the continuous-type SCW reactor are almost spherical (Fig. 2b). The differences observed in particle shape may



(a) batch SCW



(b) continuous SCW

Fig. 2. SEM photographs of synthesized YAG : Eu phosphors in (a) the batch-type (Eu conc.: 10 at%, pH: 9.41), and (b) the continuous-type SCW reactors (Eu conc.: 10 at%, reaction time: 20 s, pH: 9.10) [15,16].

result from the time and phase transition required to reach the SCW reaction condition. In case of the batch-type SCW method, a certain period of time was necessary in order to transition from ambient to SCW conditions. As a result, the longer reaction time can contribute to the growth of the phosphors. In addition, the phase transition from liquid to supercritical phases occurs during the reaction. Therefore, it is hard to control the shape of the phosphors in the heterogeneous liquid phase, and difficult to determine when the phosphors begin to undergo synthesis and whether the phosphors are synthesized at hydrothermal or SCW conditions.

Conversely, in the continuous-type SCW method, because the liquid solution at high temperature can be immediately injected into SCW conditions, the particle is synthesized under almost homoge-

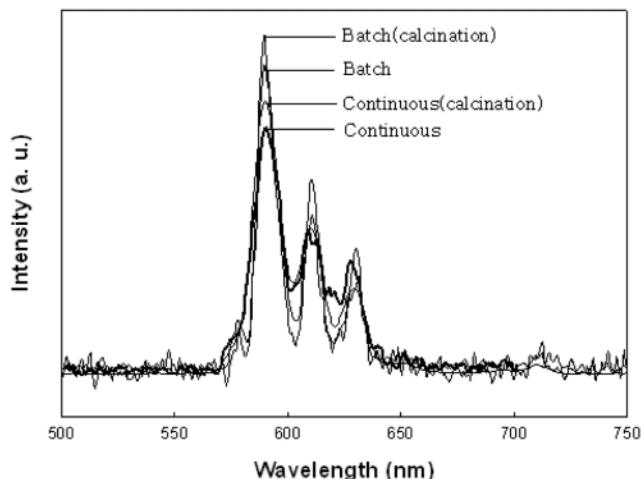


Fig. 3. Effects of calcinations on the luminescence intensities of YAG : Eu phosphors synthesized by the batch-type (Eu conc.: 10 at%, pH: 9.41) and the continuous-type SCW methods (Eu conc.: 10 at%, reaction time: 20 s, pH: 9.10).

neous SCW conditions. Moreover, due to a very short reaction time and low solubility in SCW, very small sizes of the phosphor particles were obtained. In addition, regular spherical particles were synthesized because the nuclei can be instantly immersed in SCW by mixing [16].

In Fig. 3, the photoluminescence spectra of YAG : Eu phosphors synthesized by using batch-type and continuous-type methods are compared. The YAG : Eu phosphors synthesized from both methods demonstrated the most intense emission spectra in the red spectral region upon excitation by UV light at 235 nm. The emission intensity of YAG : Eu phosphors formed by the batch-type SCW method was slightly stronger than the emission intensity of the phosphors generated by the continuous-type SCW method. It is expected that larger particles obtained from the batch-type method led to higher emission intensity.

In order to improve the luminescence performance of the synthesized YAG : Eu phosphors, the particles were calcined at 1,000 °C for 10 h before the photoluminescence spectra were measured. In Fig. 3, the effects of calcinations on the luminescence intensities of the YAG : Eu particles synthesized by batch-type and continuous-type SCW methods are illustrated. As shown in this figure, for both the batch-type and continuous-type SCW methods, the luminescence intensities were slightly enhanced by the process of calcination. These improvements may result from the removal by calcination of impurities remaining in the YAG : Eu phosphors. In addition, even through the calcination process, the gap in intensity between the batch-type and continuous-type SCW methods was apparently maintained. The gap may result from the difference in the particle sizes of both types of YAG : Eu particles synthesized.

Considering all factors investigated, it is concluded that the continuous-type SCW method is superior to the batch-type SCW method from the viewpoint of the particle size and shape. However, slightly better luminescence property of phosphors with such larger particle size can be obtained from the batch-type method. Nevertheless, either SCW method can be successfully applied to the synthesis of YAG : Eu phosphors having good luminescence properties.

CONCLUSIONS

In this study, YAG : Eu phosphors were synthesized by batch-type and continuous-type SCW methods, and their XRD patterns, SEM images, and photoluminescence spectra were compared. As a result, pure YAG particles were successfully synthesized under basic pH conditions in both SCW methods without forming by-products. The particle size of YAG : Eu phosphors generated from the continuous-type SCW method was much smaller than the particle size formed from the batch-type SCW method. In the batch-type SCW method, needle-like or elliptical-like shapes were formed, apparently resulting from the time required to reach SCW conditions from ambient conditions. However, using the continuous-type SCW method, regular spherical particles were obtained because the nuclei were instantly immersed in SCW by a mixing effect. On the other hand, the emission intensity of YAG : Eu phosphors formed by the batch-type SCW method was stronger than that the intensity of particles formed by the continuous-type SCW method. In addition, when a calcination process was applied to batch-type and continuous-type SCW methods, the luminescence intensities were slightly improved by the removal of trace impurities remaining in the YAG : Eu phosphors.

In conclusion, the continuous-type SCW method is superior to the batch-type SCW method from the viewpoint of the particle size and shape. However, the batch-type SCW method induces slightly higher luminescence intensity. Moreover, either SCW method can be successfully applied to synthesize phosphors having desirable luminescence properties.

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