Korean J. Chem. Eng., **23**(5), 842-846 (2006)

Comparison of YAG : Eu phosphor synthesized by supercritical water and solid-state methods in a batch reactor

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(*Received 12 August 2005 • accepted 7 April 2006*)

Abstract–Phosphor yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) doped with Eu (10 at%) was synthesized by supercritical water (SCW) and solid-state methods in a batch reactor. The crystals, morphologies and luminescent properties of the phosphors obtained from different pH conditions in the SCW were studied. Pure YAG phase was successfully synthesized at the alkaline condition in the SCW without formation of intermediate phases, while the size and luminescent property of YAG : Eu were strongly affected by pH condition. The luminescent intensity of YAG : Eu by the SCW method without further thermal treatment is stronger than that by the solid-state method with thermal treatment.

Key words: Supercritical Water, $Y_3Al_5O_{12}$ (YAG), Luminescent Properties

INTRODUCTION

Recently, inorganic phosphors have been extensively investigated for use in display panel applications of various types, such as the plasma display panels (PDP), vacuum fluorescent displays (VFD), and field emission displays (FED) [Kang et al., 1999]. Yttrium aluminum garnet (YAG) is a well known inorganic compound which has excellent chemical, physical and optical properties. In addition, YAG is often used as the host material of full color phosphors by doping materials such as Eu, Tb, Cr, Dy, Ce, Sm and Tm [Van der Weg et al., 1981, 1985]. Therefore, YAG based phosphors have been used widely in the field of luminescence [Lopez et al., 1997] because of their stability at conditions of high irradiance with an electron beam [Li et al., 2004].

Generally, YAG phosphors are prepared at high temperatures for an extended time period via a solid-state reaction process [Jia et al., 1994]. However, the traditional process has some disadvantages, such as the high temperature firing over an extended time period required for crystallization and the repeated grinding and milling process. In addition, phosphor particles prepared through conventional solid-state reactions have large size on the order of 5-20 μm [Li et al., 2004].

To overcome the drawbacks, various synthesis methods have been applied extensively. These include hydrothermal synthesis [Hakuta et al., 2003], sol-gel method [Yamaguchi et al., 1990; Gowada, 1986; Hay, 1993], spray-pyrolysis synthesis [Nyman et al., 1997; Jung et al., 2004], combustion process [Shea et al., 1996; Kingsley and Patil, 1988; Shikao and Jiye, 2001], and co-precipitation method [Zhou et al., 2004].

Recently, SCW has gained attention to synthesize functional inorganic materials as an excellent media. It is well known that the properties of water, such as its density, viscosity, diffusivity and static dielectric constant, are changed dramatically with slight variations of temperature and pressure at its near critical point. However, the static dielectric constant of SCW is close to that of non-polar solvents because of its minuscule value (supercritical condition <2; atmospheric condition ≈80) [Lee et al., 2004]. At the near-critical point of water, the rate of hydration (hydrothermal reaction) of metal salts increases as its dielectric constants decrease, while the solubility of metal oxide decreases rapidly as well [Hakuta et al., 2003; Nam and Kim, 2004].

In this study, YAG:Eu phosphor particles were synthesized by using batch-type SCW method (>374 °C, and >221 bar) at various pH conditions. The photoluminescence characteristics of YAG : Eu particles prepared by SCW method were measured and compared with those by a conventional solid-state method.

EXPERIMENTAL

1. Materials

Yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$: Strem Chemicals : 99.9% purity), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$: Wako Chemicals : 99.9% purity) and europium nitrate hexahydrate ($Eu(NO_3)_3 \cdot 6H_2O$: Strem Chemicals : 99.9% purity) were used as raw materials in the study. Deionized water was used after purging the solution with N_2 to remove dissolved O_2. The starting solution was prepared by dissolving these metal nitrates in the deionized water at room temperature. The yttrium nitrate hexahydrate, aluminum nitrate nonahydrate and europium nitrate hexahydrate were combined to yield a composition with the general formula $(Y_{1-x}Eu_x)_3Al_5O_{12}$ at x=0.1. An aqueous potassium hydroxide solution (KOH : Aldrich Chemicals : 99.99% purity) was then added to the starting solution, which led to alkaline conditions. The pH conditions of solution were 7.16, 9.41, and 11.21. An amount of potassium hydroxide was added to satisfy the pH conditions of solution. As the solubility of the metal hydroxide increased with temperature under basic conditions, the nucleation of YAG could begin taking place at high levels of supersaturation until reaching SCW conditions [Yamaguchi et al., 1990]. Thus, resulting particles were formed simply in this solution with the SCW.

2. Synthesis of YAG : Eu

The synthesis of YAG : Eu was performed at 300 bar and 400 °C in a batch-type SCW reactor without a mixer, as shown in Fig. 1.

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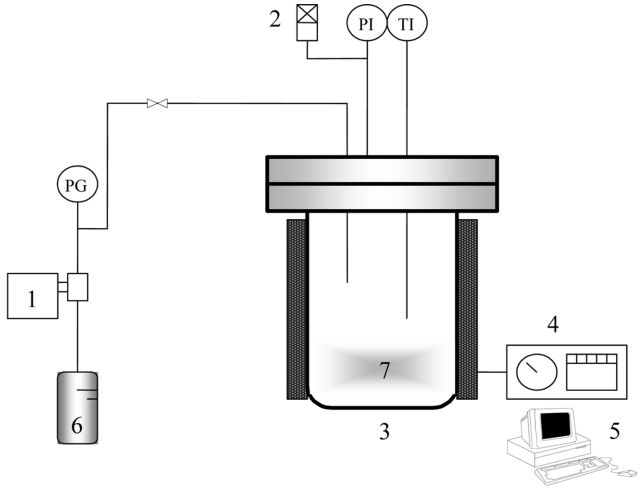


Fig. 1. Schematic diagram of experimental batch SCW apparatus.

1. High pressure pump	6. H_2O
2. Safety valve	7. Raw material
3. Reactor	PI. Pressure Indicator
4. Heater controller	TI. Temperature Indicator
5. Data recorder	PG. Pressure Gauge

The diameter of the cylindrical reactor is 6 cm i.d., 14 cm o.d. and the length of the reactor is about 13.7 cm. Stoichiometric amounts (YAG : 0.1Eu) of the starting solution and potassium hydroxide solution were mixed with deionized water of 200 ml at ambient temperature. The concentration of yttrium nitrate and aluminum nitrate was 0.015 M and 0.25 M, respectively. The pH values of resulting suspension were measured by pH meter. Then, the resulting suspension in the batch reactor was heated to the desired temperature (400 °C) and kept at that temperature for 2 h. During the reaction period, the pressure gradually increased up to 300 bar. When the reaction was finished, it was cooled to room temperature. The resulting suspension was filtered by using suction filtration and the particles were dried in an oven at 105 °C for one day.

In the solid-state method, the starting materials were mixed with a few drops of ethanol. After the mixture was milled thoroughly in an agate mortar, it was kept in a furnace for crystallization firstly at 400 °C for 2 h in air. Then, it was calcined at 1,000 °C for 4 h in air to enhance both the degree of crystallization and the luminescence intensity of the products. Repeated milling was needed between the two treatments for higher homogeneity.

A flow diagram of SCW and solid-state methods is shown in Table 1.

3. Characterization

Generally, the luminescent properties of phosphor depend on the characteristics of the particles such as crystallinity, size, shape, number of defects, and so on. The crystalline properties of the particles were identified by using X-ray diffraction (XRD, Rigaku D/max-III) analysis with CuKα radiation in the range of 2θ=10-80°. The size and morphology of the particles were analyzed with a scanning electronic microscope (SEM, Hitachi Corp., S-4200). Excitation and luminescence spectra were measured with a luminescence spectrometer (PERKIN-ELMER LS50-B) under ultraviolet (UV) light with an Xe flash lamp.

RESULTS AND DISCUSSION

1. Effect of pH Condition on YAG : Eu Phosphor in SCW Method

YAG : Eu phosphors were synthesized under three different pH conditions: 7.16, 9.41, and 11.21.

The XRD pattern of YAG : Eu phosphors synthesized under each pH condition in the batch-type SCW method was compared with the YAG standard peak in Fig. 2. The XRD peak of the synthesized phosphor in the SCW agreed well with the YAG standard peak. In addition, the difference in intensity among the particles was negligible. This implies that pure crystalline YAG can be formed successfully in the SCW method regardless of the applied pH conditions.

The SEM images of YAG : Eu phosphor under each pH condition are shown in Fig. 3. The particle size and shape of YAG : Eu phosphor synthesized at pH of 7.16 under SCW condition were widely dispersed and irregular, respectively, in Fig. 3(a). However, as

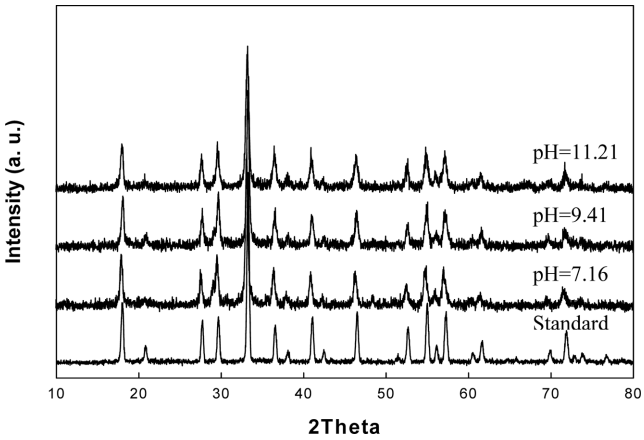
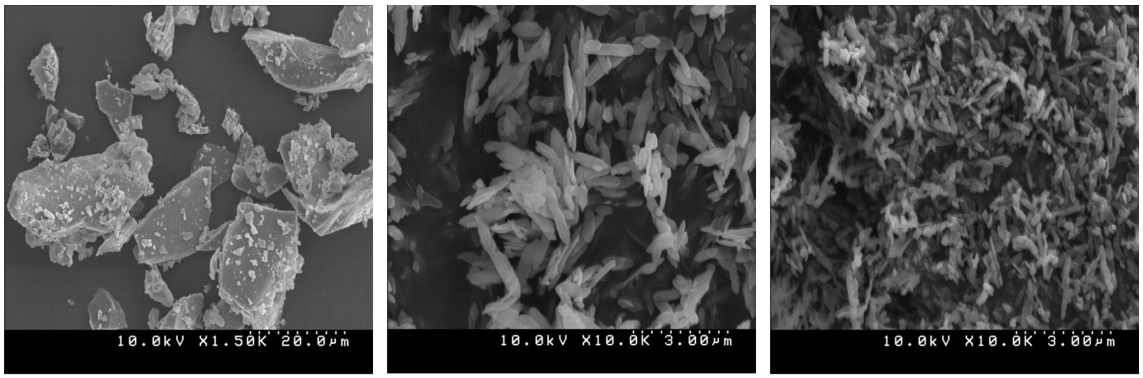


Fig. 2. XRD patterns of YAG : Eu phosphor at different pH values of SCW.

Table 1. Flow diagram for formation of phosphors by SCW and solid-state methods

	SCW (batch type)	Solid-state method
1 step	Stoichiometric amount of raw materials[$Al(NO_3)_3 \cdot 9H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$] in batch reactor+potassium hydroxide solution	Stoichiometric amount of raw materials[$Al(NO_3)_3 \cdot 9H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$] in an agate mortar+A few drops of ethanol
2 step	Reaction at 400 °C and 300 bar	Reaction during 2 h at 400 °C in air
3 step	Filtering of resulting suspension and drying	Calcination at 1,000 °C for 4 h in air
	YAG : Eu phosphor	



(a) pH = 7.16 (b) pH = 9.41 (c) pH = 11.21

Fig. 3. SEM photographs of YAG : Eu phosphor at different pH values of SCW.

shown in Figs. 3(b) and 3(c), with an increase in pH, the size of YAG : Eu phosphors in the batch-type SCW method was decreased and the phosphors were changed to needle-type and elliptical-like in shape. As observed in sol-gel [Yamaguchi et al., 1990; Gowada, 1986; Hay, 1993] and combustion [Shikao and Jiye, 2001] processes, the prepared phosphors seem to be agglomerated at high pH conditions as shown in the SEM images. However, the agglomeration at pH of 9.41 was relatively smaller than that at pH of 11.4.

The photoluminescence spectrum of YAG : Eu phosphor was measured with a luminescence spectrometer. Fig. 4 shows the emission spectra of synthesized YAG : Eu particles without further treatment. The synthesized YAG : Eu under the SCW method showed the highest excitation at 235 nm UV light, and the emission spectrum was observed in the red spectral area. Three major emission peaks were observed at 590, 608, and 628 nm, corresponding to the $^5D_0 \rightarrow {}^7F_1$ (590 nm) and $^5D_0 \rightarrow {}^7F_2$ (608 and 628 nm) transitions, which are the typical emission properties of Eu^{3+} activators. It is also noted that the $^5D_0 \rightarrow {}^7F_0$ transition for a linear crystal field at the Eu^{3+} site is not observed in the spectra. The prominent peak at 590 nm implies that the magnetic dipole transition is predominant and the Eu^{3+} ions lie in centro-symmetrical sites. And the forbidden transition of $^5D_0 \rightarrow {}^7F_2$ (608 and 628 nm) is secondary.

It is note worthy that the photoluminescence spectra of the YAG phosphors were different under each pH condition. For phosphor materials, fine particle sizes of chemical purity give high resolution, optimum chromaticity and brightness. As the solubility of the hydroxide sols increases with the temperature at basic condition, nucleation of YAG might take place at high degree of supersaturation and thus, fine particles could be more easily formed. With an increasing concentration of coexisting ions, the solubility of metal hydroxide will increase because of the decreased ion activity by an enhancement of ion strength. Since an enhancement of coexisting ions plays a role similar to that of increasing pH, fine particles could be synthesized [Hakuta et al., 2003]. The effect of pH and coexisting ions concentration on particle size could be explained by reaction equilibrium theory [Lencka and Riman, 1993]. The alkaline conditions contributed to improve the emission intensity of the YAG : Eu phosphor. However, the YAG : Eu phosphor synthesized at the pH of 9.41 showed the highest luminescent intensity. In this study, YAG : Eu phosphors prepared at the pH of 9.41 by the SCW method were compared with those by the solid-state method.

2. Comparison of YAG : Eu Phosphors Between SCW and Solid-state Methods

The XRD patterns of YAG : Eu phosphors synthesized by the

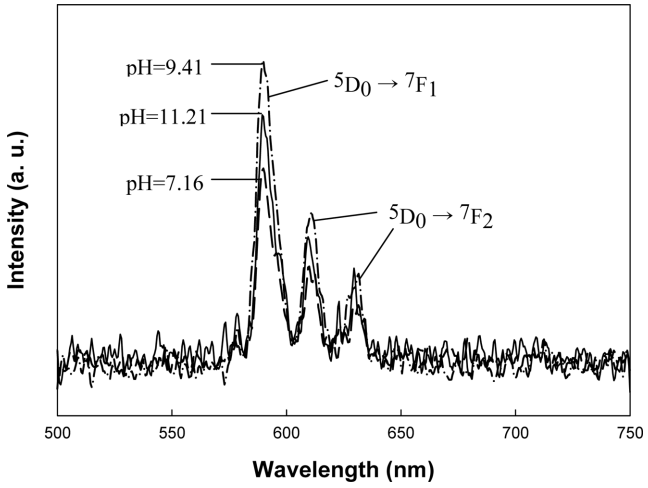


Fig. 4. Luminescence intensity (emission λ_{ex}=235 nm) of YAG : Eu phosphor at different pH values of SCW.

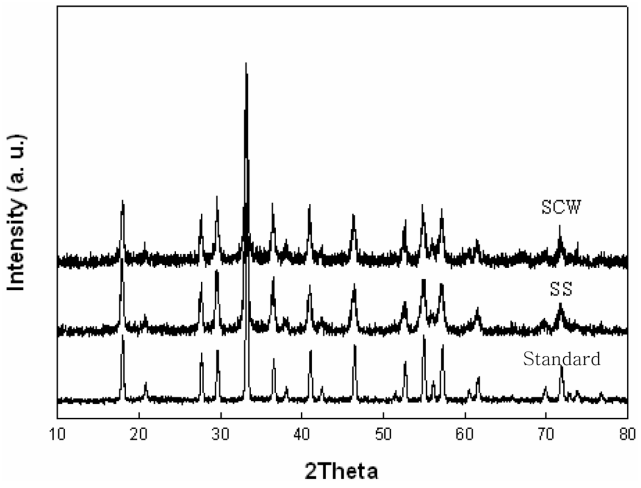
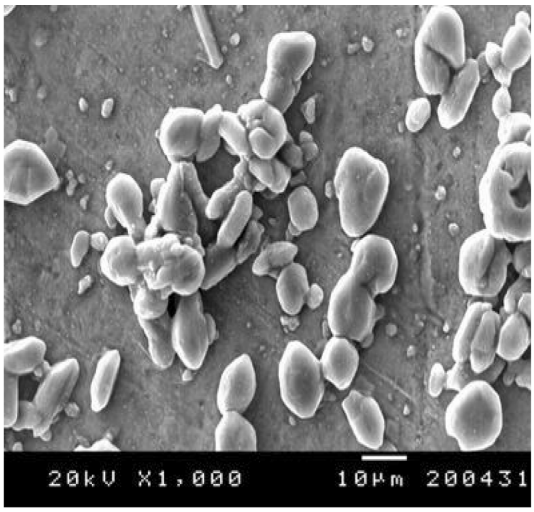


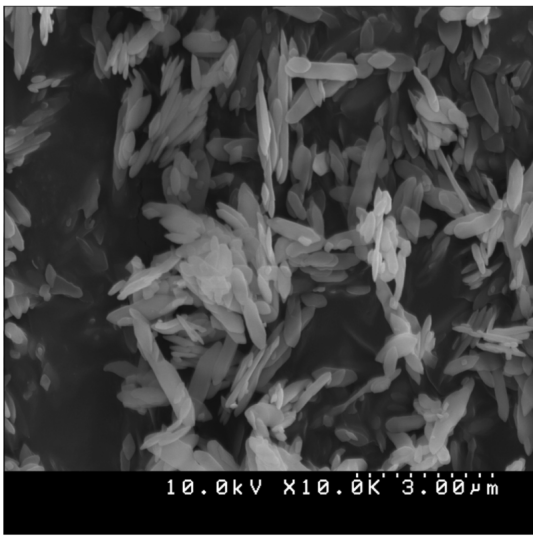
Fig. 5. XRD patterns of synthesized YAG : Eu phosphor at SCW (Conc.=Eu 10 at%, pH=9.41) and solid-state methods.

batch-type SCW and solid-state methods were compared in Fig. 5. In both methods, pure YAG phase appeared without formation of intermediate phases (YAP; $Y_4Al_2O_9$ and YAM; $YAlO_3$) and the intensity of both phosphors was similar to each other. However, repeat milling and additional heat treatment at high temperature are necessary to obtain pure YAG phase from solid-state method, whereas in the batch-type SCW method, pure YAG phase is obtained from relatively mild temperature condition without further thermal treatment.

It has been reported that phosphor materials should have a fine (<3 μm) and narrow size distribution to display strong luminescent properties [Vecht et al., 1999]. In Fig. 6, SEM images of YAG : Eu phosphors prepared by both methods were compared. The particle size of YAG : Eu phosphors sintered at 1,000 °C in the solid-state method is in the range of 5-20 μm, and their shape appears to be irregularly spherical or elliptical. From the figure, it is clearly shown that the particle size of YAG : Eu phosphors at the batch-type SCW method is much smaller. However, their needle-like or elliptical-like shape stemmed from the experimental operating condition. In the batch-type SCW method, it took time to reach from ambient condition to SCW condition. In other words, even though crystallization starts at near critical condition of water, the reaction condition still slowly changes to the desired condition without mixing. Therefore, it is expected that the spherical shape of phosphors can be synthesized in the injecting continuous system under SCW condition [In et al., 2005] because the nuclei can be immersed in the SCW in an instant.



(a) Solid state



(b) SCW

Fig. 6. SEM photographs of synthesized YAG : Eu phosphor at SCW (Conc.=Eu 10 at%, pH=9.01) and solid-state methods.

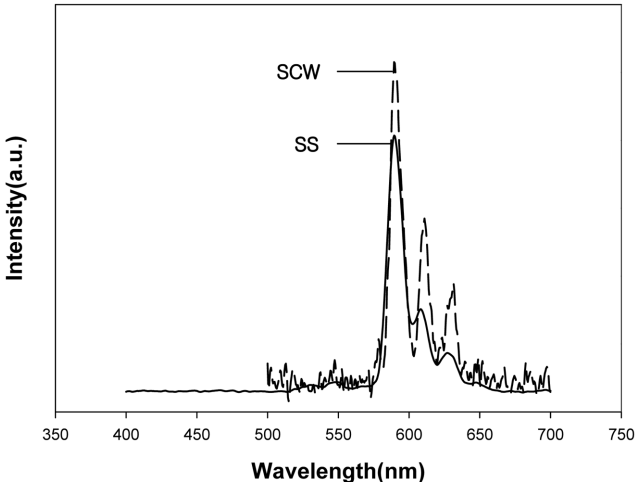


Fig. 7. Luminescence intensity (emission λ_{ex}=235 nm) of synthesized YAG : Eu phosphor at SCW (Conc.=Eu 10 at%, pH= 9.41) and solid-state methods.

The emission spectra of YAG : Eu prepared by the batch-type SCW and solid-state methods were observed in the red spectral area. As shown in Fig. 7, the emission intensity of YAG : Eu by the SCW method is stronger than that by the solid-state method. From the emission intensity of YAG : Eu phosphors, it is concluded that SCW method can be successfully applied to synthesize phosphors with good luminescence properties even though no further thermal treatment is used.

CONCLUSION

In this study, YAG : Eu phosphors were synthesized by batch-type SCW and solid-state method.

Pure YAG phase was successfully synthesized at the alkaline condition in the SCW without formation of intermediate phases. In general, solubility of metal oxide and methal hydroxide in neutral and alkali aqueous solutions increases with temperature. As the temperature is elevated, near the critical point of water (374 °C, 22.1 MPa), however, the solubility of metal oxides and hydroxides drastically decreases [Sue et al., 1999]. Hakuta and coworkers reported the dissolving recrystallization process. They reported that, after the starting hydroxide sol is miscible in water during the heating period, the particles are decomposed in supercritical water where metal oxide solubility decreases drastically through hydrothermal reaction. Then, the particles are recrystallized in supercritical water [Hakuta et al., 2003]. Therefore, in this study, it is expected that the particles started to be formed from 374 °C to 400 °C.

The synthesized YAG : Eu under the SCW method showed that the emission spectrum was observed in the red spectral area. Three major emission peaks were observed at the $^5D_0 \rightarrow {}^7F_1$ (590 nm) and $^5D_0 \rightarrow {}^7F_2$ (608 and 628 nm) transitions.

The size and luminescent property of YAG : Eu were strongly affected by the pH condition. The particle size was decreased with an increase in pH condition, while maximum luminescent intensity of YAG : Eu was obtained at pH of 9.41.

The emission intensity of YAG : Eu by SCW method without further thermal treatment is stronger than that by solid-state method with thermal treatment, which is normally treated at higher than 1,000 °C. In addition, the particle size and distribution in SCW method were smaller and narrower than those in solid-state method.

It is concluded that the SCW method can be successfully applied to synthesize phosphors with good luminescence properties. In addition, the SCW method can reduce production time for phosphors because the product does not need post-treatment and long time reactions.

ACKNOWLEDGMENTS

This subject is supported by Ministry of Environment as "The Eco-technopia 21 project" and the authors would like to thank the Ministry of Environment.

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