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Characteristics of $Y_3Al_5O_{12}$:Ce phosphor powders prepared by spray pyrolysis from ethylenediaminetetraacetic acid solution

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Abstract

Nanometer and submicron-sized YAG:Ce phosphor powders were prepared by spray pyrolysis from the spray solutions with ethylenediaminetetraacetic acid (EDTA). The precursor powders with hollow and thin wall structure turned to the fine-sized YAG:Ce phosphor powders after post-treatment at high temperatures of 1400 and 1500 °C. The mean size of the phosphor powders post-treated at a temperature of 1500 °C was 0.72 μm. The white LEDs formed from the YAG:Ce phosphor powders post-treated at 1400 and 1500 °C showed (0.2781, 0.2871) and (0.2731, 0.2795) on the CIE chromaticity diagram, and about 78.20 and 79.04 of Ra. The luminous efficiency of the white LED formed from the commercial YAG:Ce phosphor powders was 84.36 lm/W. However, the luminous efficiencies of the white LEDs formed from the YAG:Ce phosphor powders post-treated at 1400 and 1500 °C were 47.74 and 76.64 lm/W.

Keywords: A. Powders-gas phase reaction; A. Powders-chemical preparation

1. Introduction

$Y_3Al_5O_{12}$:Ce (YAG:Ce) phosphor was mainly used as yellow-emitting phosphor for white light emitting diodes (LEDs) [1,2]. YAG:Ce phosphor powders emitting yellow light had high emission efficiency under blue light. YAG:Ce phosphor powders with the mean sizes larger than 5 μm prepared by solid-state reaction method are mainly used to produce white LEDs. YAG:Ce phosphor powders are mixed with epoxy or silicon resins to deposit the powders over the LED chips. The high sedimentation velocity of YAG:Ce phosphor powders with large size produce the white LEDs with various chromaticity coordinates. The fine-sized YAG:Ce phosphor powders has also advantage in reducing an internal light scattering. Minimizing the internal light scattering might be improving the efficiency of white LEDs in displays and lighting applications.

Fine-sized YAG:Ce phosphor powders are widely studied in various liquid-solution and gas phase reaction methods [3–10]. However, fine-sized YAG:Ce phosphor powders were prepared at low post-treatment temperatures below 1300 °C in liquid solution methods. YAG:Ce phosphor powders prepared by spray pyrolysis from the spray solutions with BaF_2 flux had micron sizes at a post-treatment temperature of 1500 °C [10]. BaF_2 flux improved the morphological and optical properties of the YAG:Ce phosphor powders.

In this study, nanometer and submicron-sized YAG:Ce phosphor powders were prepared by spray pyrolysis. The precursor powders with hollow and thin wall structure were prepared by spray pyrolysis from spray solutions with ethylenediaminetetraacetic acid (EDTA) and BaF_2 flux. The precursor powders turned to the fine-sized YAG:Ce phosphor powders after post-treatment at high temperatures of 1400 and 1500 °C. The effect of EDTA on the morphological and optical properties of YAG:Ce phosphor powders prepared by spray pyrolysis were investigated.

2. Experimental

YAG:Ce phosphor powders with composition of $Y_{2.965}Al_5O_{12}$:$Ce_{0.035}$ showing the maximum photoluminescence intensity in the spray pyrolysis was prepared. A 1.7 MHz ultrasonic spray generator having six vibrators is used to generate large amount of droplets. The flow rate of air used as

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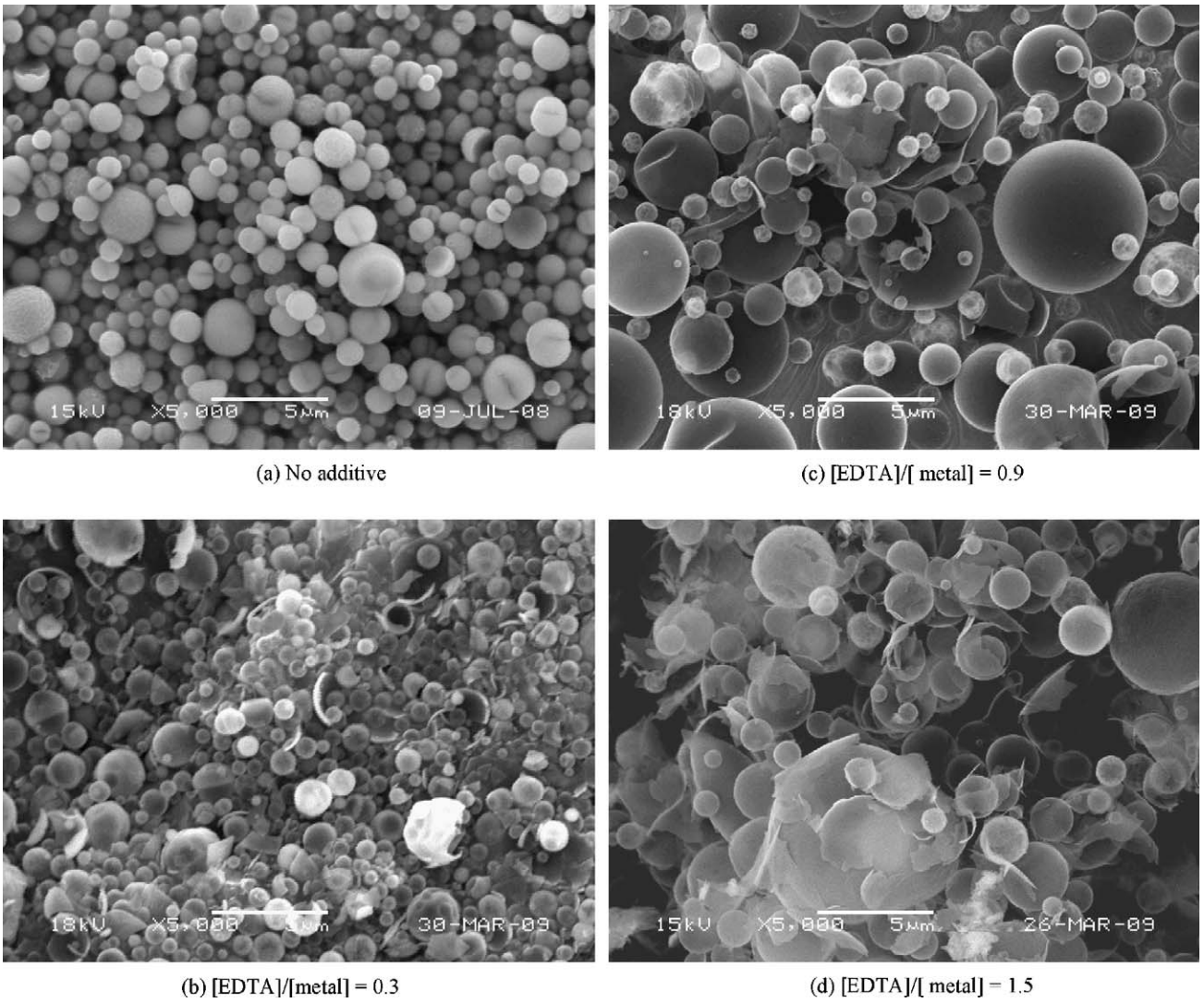


(a) No additive

(c) [EDTA]/[metal] = 0.9

(b) [EDTA]/[metal] = 0.3

(d) [EDTA]/[metal] = 1.5

Fig. 1. SEM images of as-prepared powders obtained by spray pyrolysis from spray solutions with various EDTA concentrations.

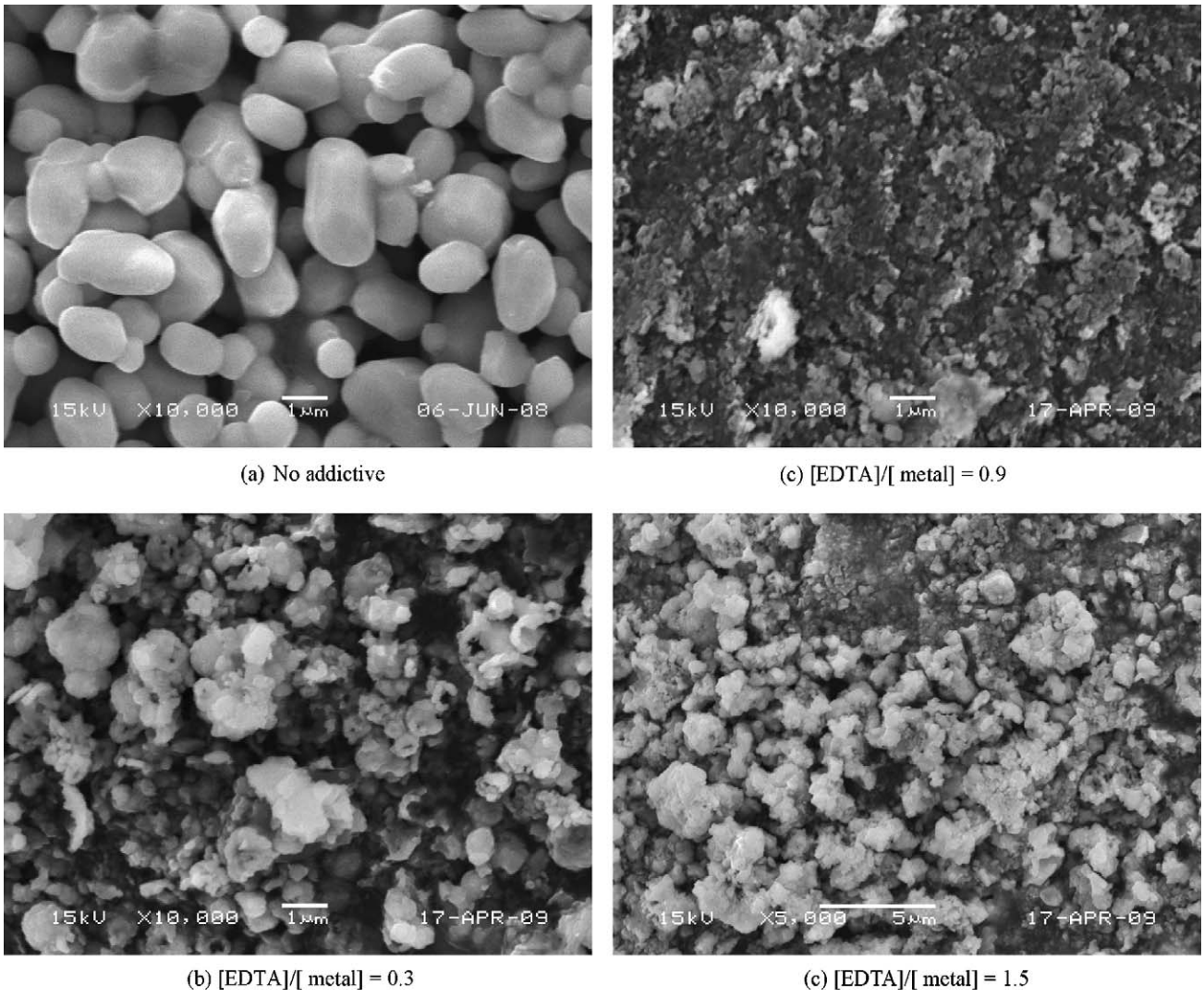
carrier gas was 40 L/min and the reactor temperature was fixed at 1000 °C. And the residence time of the powders inside the reactor was 0.5 s. The overall solution concentration of Y, Al and Ce components was 0.1 M. The amount of BaF_2 flux dissolved to the spray solution was fixed to 9 wt% of the YAG:Ce phosphor. The molar ratios of EDTA and metal components were changed from 0 to 1.5. The precursor powders obtained by spray pyrolysis were post-treated at temperatures between 1250 and 1500 °C for 5 h in 10% H_2/N_2 mixture gas.

The morphological characteristics of the powders were analyzed using scanning electron microscopy (SEM, JEOL, JSM 6060). The crystal structures of the prepared phosphor powders were analyzed using X-ray diffractometry (XRD, RIGAKU, DMAX-33). Optical properties of the phosphor powders were measured by spectrofluorophotometry (PerkinElmer LS50B) under the excitation by blue light produced by a Xe flash lamp. The white LEDs were prepared by combining the InGaN-based blue LEDs and the prepared YAG:Ce phosphor powders. The luminescence of the white LEDs under operating condition of 20 mA at room temperature was measured.

3. Results and discussion

The morphologies of the precursor powders prepared by spray pyrolysis from spray solutions with various molar ratios of EDTA and metal components are shown in Fig. 1. The precursor powders prepared from spray solution without EDTA had spherical shape and dense structure. However, the precursor powders prepared from spray solutions with EDTA had hollow morphologies and large sizes larger than 5 μm. The hollowness of the precursor powders increased with an increase of molar ratio of EDTA and metal components dissolved to the spray solutions.

Fig. 2 shows the SEM images of the YAG:Ce phosphor powders. The precursor powders prepared by spray pyrolysis from spray solutions with various molar ratios of EDTA and metal components were post-treated at a temperature of 1400 °C. The YAG:Ce phosphor powders prepared from spray



(a) No addictive

(c) [EDTA]/[metal] = 0.9

(b) [EDTA]/[metal] = 0.3

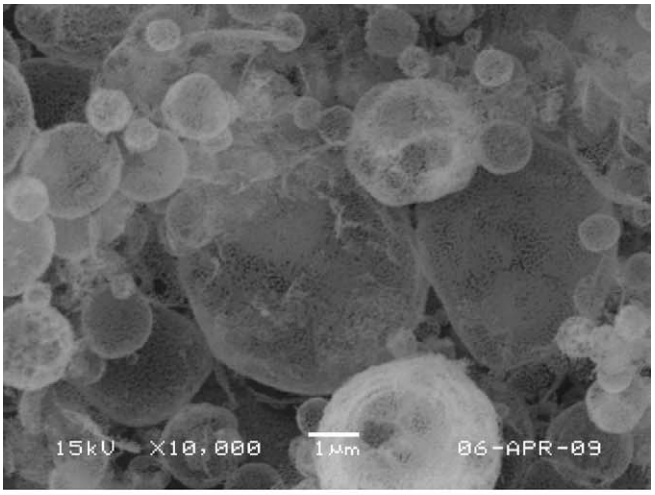
(c) [EDTA]/[metal] = 1.5

Fig. 2. SEM images of post-treated YAG:Ce phosphor powders prepared from spray solutions with various EDTA concentrations.

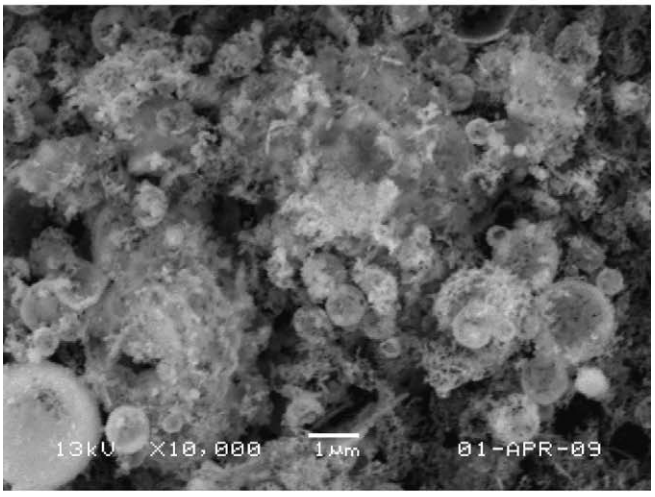
solution without EDTA had micron sizes and spherical-like morphology. The morphologies of the YAG:Ce phosphor powders were affected by the molar ratios of EDTA and metal components. The phosphor powders prepared from spray solution with low molar ratio of EDTA and metal components as 0.3 had highly aggregated morphology and irregular shape. However, the phosphor powders prepared from spray solution with an optimum molar ratio of EDTA and metal components as 0.9 had slightly aggregated morphology of the primary powders with nanometer sizes. The phosphor powders prepared from spray solution with high molar ratio of EDTA and metal components as 1.5 had also highly aggregated morphology and irregular shape.

Fig. 3 shows the SEM images of the YAG:Ce phosphor powders post-treated at various temperatures. The precursor powders prepared from spray solutions with molar ratio of EDTA and metal components as 0.9 were post-treated at temperatures between 1250 and 1500 °C. The post-treated phosphor powders were not crushed by milling apparatus. Therefore, the phosphor powders post-treated at a temperature of 1250 °C had spherical shape and aggregated structure of the primary powders with nanometer sizes. The spherical shape of the phosphor powders disappeared with an increase of the post-treatment temperatures. The phosphor powders post-treated at temperatures below 1400 °C had nanometer sizes below 100 nm in Figs. 2(c) and 3. However, growth of the particles occurred at a post-treatment temperature of 1500 °C. The phosphor powders post-treated at 1500 °C had the mean size of 0.72 μm and regular morphology.

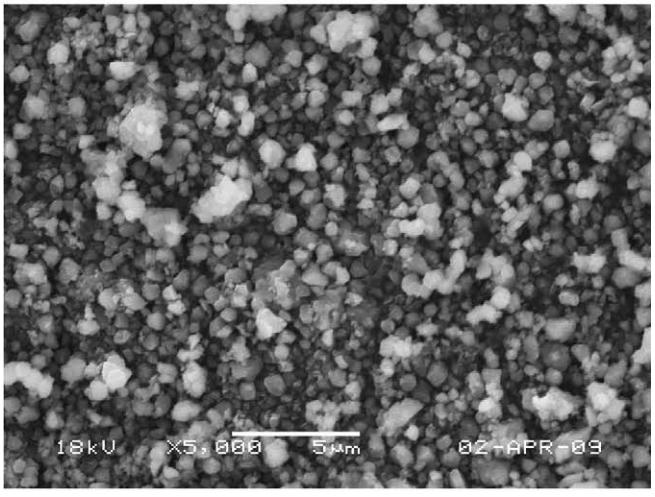
Fig. 4 shows the photoluminescence spectra of the YAG:Ce phosphor powders post-treated at various temperatures. The precursor powders prepared from spray solutions with molar ratio of EDTA and metal components as 0.9 were post-treated at temperatures between 1250 and 1500 °C. The photoluminescence intensity of the prepared phosphor powders were compared to that of the commercial YAG:Ce phosphor powders. The mean size of the commercial phosphor powders prepared by solid-state reaction method applying flux material was 17 μm. The prepared phosphor powders were excited by a long-wavelength blue-emitting light of 455 nm. The prepared YAG:Ce phosphor powders had broad emission spectra between 500 and 670 nm, with maximum peak intensity at



(a) 1250 °C



(b) 1350 °C



(c) 1500 °C

Fig. 3. SEM images of YAG:Ce phosphor powders post-treated at various temperatures.

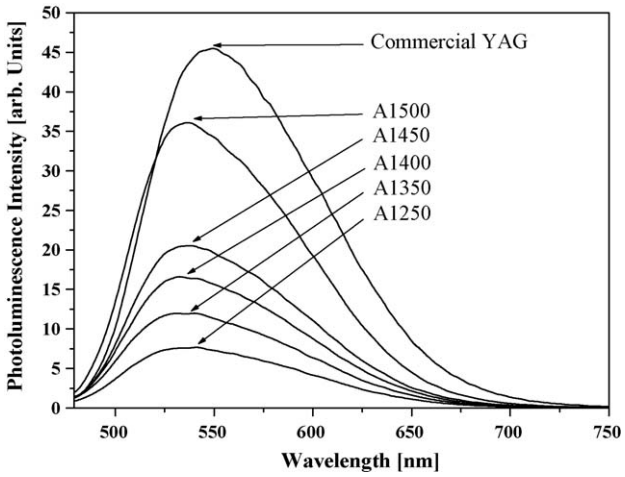


Fig. 4. Emission spectra of YAG:Ce phosphor powders post-treated at various temperatures.

532.5–541.5 nm according to the post-treatment temperatures. The photoluminescence intensities of the prepared YAG:Ce phosphor powders increased with an increase of the post-treatment temperatures. The decrease of surface defects by increasing the mean sizes and crystallite sizes of the phosphor powders according to the increasing of the post-treatment temperatures improved the photoluminescence intensities. The relative photoluminescence intensity of the phosphor powders post-treated at an optimum temperature of 1500 °C was 79.4% of that of the commercial phosphor powders. However, the relative photoluminescence intensity of the nano-sized phosphor powders post-treated at 1250 and 1400 °C were 16.8 and 36.5% of that of the commercial phosphor powders.

The white LEDs were prepared by combining the InGaN-based blue LEDs and the prepared YAG:Ce phosphor powders. The luminescence of the white LEDs under operating condition of 20 mA at room temperature was measured. Fig. 5 shows the emission spectra of the white LEDs. The spectra of the white LEDs formed from the YAG:Ce phosphor powders post-treated

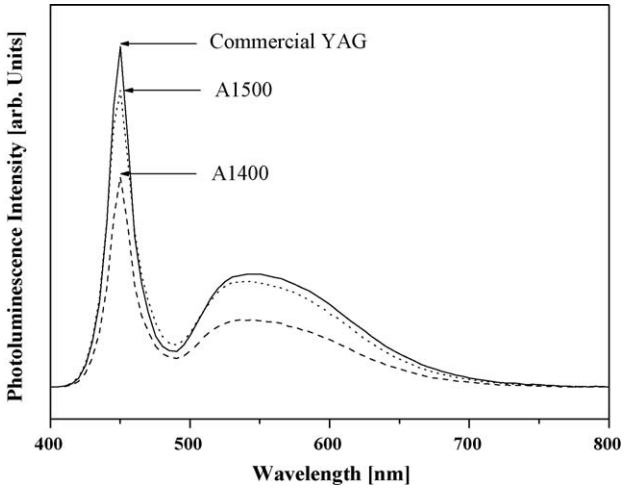


Fig. 5. Emission spectra of the white LEDs (SMD type) using both InGaN-based blue LEDs and YAG:Ce phosphor powders.

Table 1
Optical properties of white LEDs prepared by combining the InGaN-based blue LEDs and the prepared YAG:Ce phosphor powders.

Samples	CIE color coordinates		Ra	Efficiency [lm/W]
	x	*y*		
A1400	0.2781	0.2871	78.20	47.74
A1500	0.2731	0.2795	79.04	76.64
Commercial	0.2792	0.2810	79.78	84.36

at 1400 and 1500 °C were compared to that of the white LED formed from the commercial YAG:Ce phosphor powders. Optical properties of the white LEDs are summarized in Table 1. Two distinct emission bands from blue LED and yellow phosphors are clearly resolved at 450 nm and at around 540 nm, respectively. The white LED formed from the commercial YAG:Ce phosphor powders showed (0.2792, 0.2810) on the CIE chromaticity diagram, and about 79.78 of Ra. However, the white LEDs formed from the YAG:Ce phosphor powders post-treated at 1400 and 1500 °C showed (0.2781, 0.2871) and (0.2731, 0.2795) on the CIE chromaticity diagram, and about 78.20 and 79.04 of Ra. The luminous efficiency of the white LED formed from the commercial YAG:Ce phosphor powders was 84.36 lm/W. However, the luminous efficiencies of the white LEDs formed from the YAG:Ce phosphor powders post-treated at 1400 and 1500 °C were 47.74 and 76.64 lm/W.

4. Conclusions

Characteristics of fine-sized YAG:Ce phosphor powders prepared by spray pyrolysis from the spray solutions with ethylenediaminetetraacetic acid (EDTA) were investigated. EDTA added to the spray solutions enabled the formation of fine-sized YAG:Ce phosphor powders. The optimum molar ratio of EDTA and metal components to prepare the YAG:Ce phosphor powders with fine size and high photoluminescence intensity was 0.9. The YAG:Ce phosphor powders prepared by spray pyrolysis at a post-treatment temperature of 1500 °C had lower photoluminescence intensities than that of the commercial YAG:Ce phosphor powders prepared by solid-state reaction method. However, the white LED formed from the prepared YAG:Ce phosphor powders had similar CIE chromaticity and luminous efficiency to those of the white LED formed from the commercial YAG:Ce phosphor powders with the mean size of 17 μm.

References

[1] S. Nakamura, G. Fasol, The Blue Laser Diode, Springer, Berlin, 1996.
[2] Y. Uchida, T. Setomoto, T. Taguchi, Y. Nakagawa, K. Miyazaki, in: I.-W. Wu, H. Uchiike (Eds.), Display Technologies, vol. 4079, The International Society for Optical Engineering Bellingham, WA, 2000, p. 120.
[3] Y.C. Kang, I.W. Lenggoro, S.B. Park, K. Okuyama, YAG:Ce phosphor particles prepared by ultrasonic spray pyrolysis, Mater. Res. Bull. 35 (2000) 789–798.
[4] X. Li, H. Liu, J. Wang, H. Cui, F. Han, YAG:Ce nano-sized phosphor particles prepared by a solvothermal method, Mater. Res. Bull. 39 (2004) 1923–1930.
[5] K.Y. Jung, H.W. Lee, Enhanced luminescent properties of $Y_3Al_5O_{12}$:Tb^{3+},Ce^{3+} phosphor prepared by spray pyrolysis, J. Lumin. 126 (2007) 469.
[6] Y.P. Fu, S.B. Wen, C.S. Hsu, Preparation and characterization of $Y_3Al_5O_{12}$:Ce and Y_2O_3:Eu phosphors powders by combustion process, J. Alloys Compd. 458 (2008) 318–322.
[7] H.M.H. Fadlalla, C.C. Tang, YAG:Ce^{3+} nano-sized particles prepared by precipitation technique, Mater. Chem. Phys. 114 (2009) 99–102.
[8] H.S. Yang, D.K. Lee, Y.S. Kim, Spectral variations of nano-sized $Y_3Al_5O_{12}$:Ce phosphors via codoping/substitution and their white LED characteristics, Mater. Chem. Phys. 114 (2009) 665–669.
[9] Y. Zhou, J. Lin, M. Yu, S. Wang, H. Zhang, Synthesis-dependent luminescence properties of $Y_3Al_5O_{12}$:Re^{3+} (Re = Ce, Sm, Tb) phosphors, Mater. Lett. 56 (2002) 628–636.
[10] S.H. Lee, D.S. Jung, J.M. Han, H.Y. Koo, Y.C. Kang, Fine-sized $Y_3Al_5O_{12}$:Ce phosphor powders prepared by spray pyrolysis from the spray solution with barium fluoride flux, J. Alloys Compd. 477 (2009) 776–779.