

# Preparation with Laser Ablation and Photoluminescence of $Y_3Al_5O_{12}:Ce$ Nanophosphors

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We prepared  $Y_3Al_5O_{12}:Ce$  (YAG:Ce) nanophosphors with a mean size of 15 nm by using laser ablation of micron-sized commercial YAG:Ce target phosphor in 1,4-butanediol. The photoluminescence properties of the YAG:Ce nanophosphors were compared with those of micron-sized YAG:Ce phosphor. The elimination of back-scattering effect was confirmed by the optical properties of the YAG:Ce nanophosphors. The thermal stability of the YAG:Ce nanophosphors was also examined for the use of high power white LED. We convinced that the laser ablation method in 1,4-butanediol is an adequate method for the preparation of YAG:Ce nanophosphors for high power white LED with enhancement of the transmittance of the blue light from the InGaN chip.

**Keywords:** photoluminescence,  $Y_3Al_5O_{12}:Ce$ , laser ablation, nanophosphor, white LED

## 1. INTRODUCTION

The energy consumption of a white LED is only approximately 20% of that of bulk light. White LEDs are also considered to be life-long lighting sources, since their lifetime is approximately 100,000 h. Moreover, white LEDs do not contain harmful materials, in contrast to fluorescent lamps, for instance, which contain mercury. Therefore, white LEDs are considered to be among the most promising lighting sources.<sup>[1-3]</sup> However, higher power white LEDs are still required if they are to be competitive from the point of view of cost with commercial fluorescent lamps.

Commercial white LEDs are fabricated by coating a yellow-emitting  $Ce^{3+}$ -doped yttrium aluminum garnet ( $Y_3Al_5O_{12}:Ce$ , YAG:Ce) phosphor onto a blue-emitting InGaN LED chip.<sup>[4,5]</sup> YAG:Ce is a well-known phosphor that emits yellow light and is excited by UV and blue light. White light is obtained from white LEDs because of the mixing of the yellow emission of the YAG:Ce phosphor with the unabsorbed blue emission of the blue-emitting InGaN LED chip. To develop higher power white LEDs, brighter YAG:Ce phosphors are needed. In general, YAG:Ce is synthesized by carrying out the solid-state reaction of  $Y_2O_3$ ,  $Al_2O_3$ , and  $CeO_2$  at high temperatures in the range 1400°C to 1700°C.<sup>[6,7]</sup> A few micron-sized YAG:Ce phosphors are usually prepared in this solid state reaction. A variety of approaches to the preparation of YAG:Ce phosphors with brighter emission have been investigated: the control of the reaction temperature or reaction

time, and the use of different precursors, different amounts of  $Ce^{3+}$  ions, and different fluxes.<sup>[8-10]</sup> The synthetic conditions for optimal emission are now well known. Therefore, we require new types of YAG:Ce phosphors to produce higher power white LEDs.

The phosphors prepared with the solid state reaction are micron-sized and thus induce the back-scattering of the blue emission from the blue LED chips. Some portions of the blue emission are lost in this back-scattering process. Nano-sized phosphors with less back-scattering are needed for high power white LEDs. In recent years, YAG:Ce nanophosphors have been synthesized by using organic surfactants as soft templates. However, these organic surfactants, which cap the YAG:Ce nanoparticles, slowly decompose at moderate temperatures above 200°C. The photoluminescence intensities of YAG:Ce nanoparticles prepared with organic surfactants slowly decrease with operation time. In the case of a high power white LED, the temperature inside its epoxy capsule increases up to the moderate temperature of 160°C. As a result, YAG:Ce nanophosphors prepared with soft templates in the bottom-up method are not adequate for high power white LEDs. Recently, crystalline nanoparticles have been prepared by using laser ablation.<sup>[11-14]</sup> There are only a few reports of the preparation of YAG:Ce nanophosphors by using laser ablation in aqueous solution as a top-down method.<sup>[15,16]</sup> In this paper, we present a simple laser ablation method for the preparation of YAG:Ce nanophosphors in 1,4-butanediol without any organic surfactants. We also investigated the photoluminescence properties of the YAG:Ce nanophosphors prepared with laser ablation.

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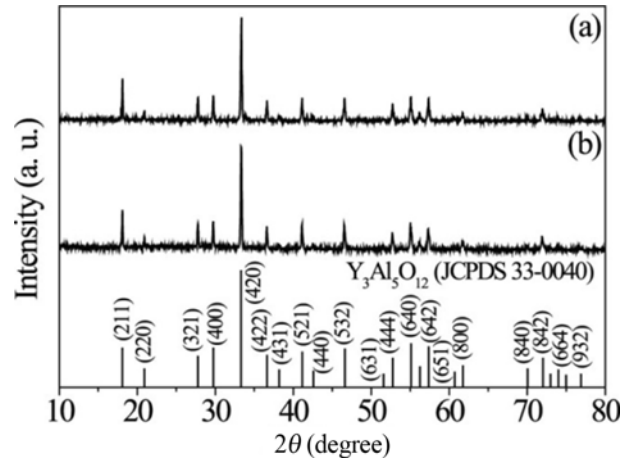
## 2. EXPERIMENTAL PROCEDURE

The commercial YAG:Ce phosphor was obtained from Phosphor Tech. Ltd. YAG:Ce nanophosphors were synthesized by performing the pulsed laser ablation of the YAG:Ce target phosphor. The YAG:Ce target phosphor was fabricated with the hot press method: the commercial YAG:Ce phosphor (Phosphor Tech. Ltd.) was poured into a mold and sintered at 1500°C for 2 h in air under a pressure of 1 ton/cm<sup>2</sup> with a heating rate of 5°C/min. Pulsed laser ablation was performed by focusing third harmonic Nd:YAG laser (355 nm, Continuum Surelite) pulses, perpendicularly aligned to the pellet surface and operating at a repetition rate of 10 Hz, by means of a lens with a focal length of 25 cm. The laser pulse energy was set at 100 mJ with a laser spot of approximately 1 mm. The target was placed at the bottom of a 100 mL beaker and covered with 60 mL of 1,4-butanediol. The depth of the solution layer above the target was approximately 10 mm. The target was stirred and ablated during laser irradiation for 6 h at room temperature. The product was centrifuged at 11000 rpm for 30 min, washed several times with ethanol, and dried at 60°C for 12 h. 0.05 g of the YAG:Ce nanophosphors was dispersed in 2 mL of toluene in a 10 mL vial for 10 min. 2.0 g of PAS (Series 800, Jujo) ink was dispersed into the above mixture and stirred for 10 min. The YAG:Ce nanophosphor suspension was coated onto a commercial overhead transparency film to a thickness of 90 μm by using an applicator.

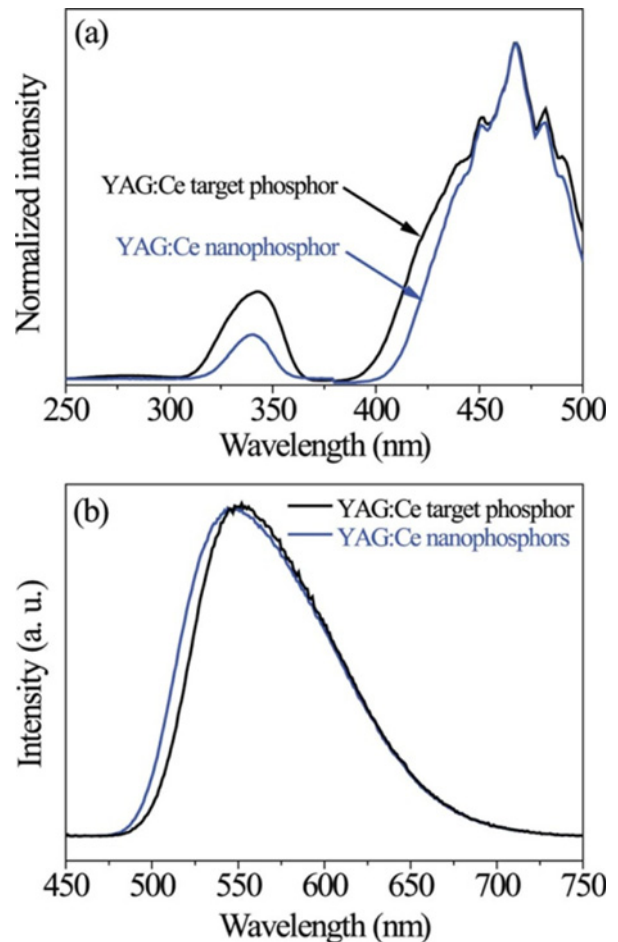
The excitation and emission spectra of the YAG:Ce phosphors were obtained by using a spectrum analyzer (DARSA, PSI). The excitation spectra were obtained by fixing the emission wavelength ( $\lambda_{em}$ ) at 550 nm. The emission spectra were obtained by fixing the excitation wavelength ( $\lambda_{ex}$ ) at 465 nm, which is the wavelength of the commercial blue-emitting InGaN LED chip. Powder x-ray diffraction (XRD, Rigaku DMAX-3A) with Cu K $\alpha$  radiation was used to examine the crystal structures of the YAG:Ce phosphors. Scanning electron microscopy (SEM, Hitachi S-4300) and high resolution transmission electron microscopy (HRTEM, JEOL JEM-3010) were carried out to investigate the morphologies of the YAG:Ce phosphors.

## 3. RESULTS AND DISCUSSION

Figure 1 shows x-ray diffraction (XRD) patterns of the YAG:Ce bulk target phosphor obtained from Phosphor Tech., pressed into a pellet by applying a pressure of 1 ton/cm<sup>2</sup> and sintered at 1500°C for 2 h, and of YAG:Ce nanophosphors prepared with laser ablation in 1,4-butanediol. All the XRD peaks of the target phosphor and the nanophosphors are in perfect agreement with those for the cubic crystal structure of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (JCPDS 33-0040), with  $a = 1.2016$  nm. The crystal structure of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce is almost identical to that of



**Fig. 1.** XRD patterns of (a) the YAG:Ce target phosphor obtained from Phosphor Tech. Ltd. and (b) the YAG:Ce nanophosphors prepared with laser ablation.



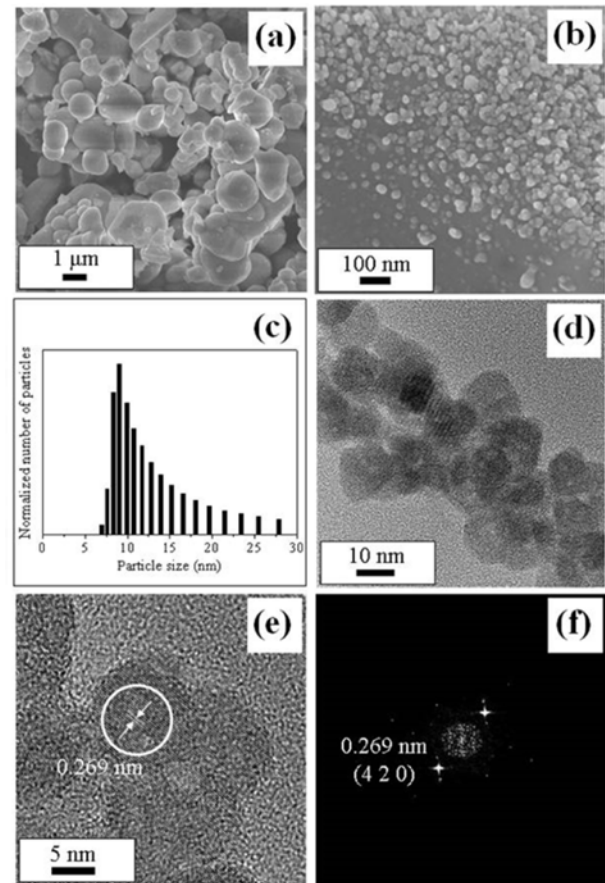
**Fig. 2.** (a) Excitation and (b) emission spectra of the YAG:Ce target phosphor and the YAG:Ce nanophosphors prepared with laser ablation. The excitation spectra were obtained by fixing the emission wavelength at 550 nm. The emission spectra were obtained by fixing the excitation wavelength at 465 nm, which is the exact wavelength of the blue-emitting InGaN chip.

$\text{Y}_3\text{Al}_5\text{O}_{12}$  because the  $\text{Ce}^{3+}$  ions (0.101 nm) occupy the  $\text{Y}^{3+}$  ion (0.090 nm) sites.<sup>[17]</sup>  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{YAlO}_3$  (YAP, yttrium aluminum perovskite), and  $\text{Y}_2\text{Al}_4\text{O}_9$  (YAM, yttrium aluminum monoclinic) were not formed during the laser ablation process.

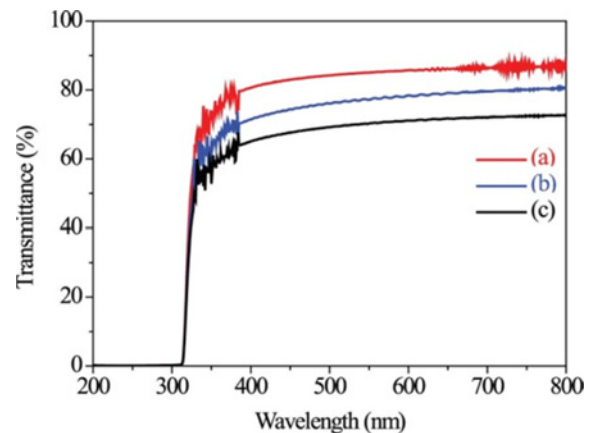
Figures 2(a) and (b) show the excitation and emission spectra respectively of the YAG:Ce target phosphor and the nanophosphors prepared with laser ablation. The emission intensity of the YAG:Ce nanophosphors prepared with laser ablation is almost equal to that of the target YAG:Ce phosphor. This result indicates that the photoluminescence intensity does not decrease as a result of the formation of nanoparticles.

In general, photoluminescence intensities decrease with the formation of smaller nanophosphors due to the formation of larger defective surface areas. However, crystal surface defects are not evident in the emission spectra of the YAG:Ce nanophosphors prepared with laser ablation. Therefore, the laser ablation technique is an adequate method for the preparation of nanophosphors without unacceptable loss of luminescence properties. The excitation spectra contain a large broad band between 400 nm and 500 nm. There is strong absorption at 465 nm, which is the emission wavelength of the commercial blue InGaN chip, as shown in Fig. 2(a). The emission spectra contain a broad band around 550 nm that originates from the  $5d^1(t_{2g}) \rightarrow 4f^1$  transition of the  $\text{Ce}^{3+}$  ion in  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ , as shown in Fig. 2(b). The broad emission spectra are due to the two electronic states of  $4f^1$  with  $^2F_{7/2}$  and  $^2F_{5/2}$  term symbols formed by spin-orbit interactions.<sup>[18]</sup> Moreover, the  $d \rightarrow f$  transition of the  $\text{Ce}^{3+}$  ions is parity allowed, so YAG:Ce is an efficient yellow emitting phosphor, which means that the YAG:Ce nanophosphors prepared with the laser ablation technique can be used as yellow-emitting phosphors excited by the blue InGaN chip in a phosphor-converted white LED.

Figure 3(a) shows a scanning electron microscopy (SEM) image of the YAG:Ce target phosphor. Polygonal crystals with a mean size of  $1.5 \mu\text{m}$  are evident. Figure 3(b) shows an SEM image of a YAG:Ce nanophosphor prepared with laser ablation, which confirms that nano-sized crystals are formed by the laser ablation process. Figure 3(c) shows a histogram of the particle size distribution of the YAG:Ce nanoparticles. The size of the nanoparticles is in the range 6 nm to 28 nm. The mean size of the YAG:Ce nanophosphors is 15 nm, which is sufficiently smaller than 50 nm to eliminate back-scattering.<sup>[19]</sup> Figures 3(d) and (e) show high resolution transmission electron microscopy (HRTEM) images with low and high magnifications respectively of the YAG:Ce nanophosphors. The high magnification HRTEM image of an individual YAG:Ce nanophosphor shows that there is a lattice spacing between the adjacent layers of 0.269 nm, which corresponds to the (420) plane of a cubic  $\text{Y}_3\text{Al}_5\text{O}_{12}$  crystal. The fast Fourier transform (FFT) patterns of the



**Fig. 3.** SEM images of (a) the YAG:Ce target phosphor and (b) a YAG:Ce nanophosphor prepared with laser ablation. (c) Histogram of the size distribution of YAG:Ce nanophosphors prepared with laser ablation. (d) Low magnification and (e) high magnification TEM images of the YAG:Ce nanophosphors prepared with laser ablation. (f) FFT patterns of the YAG:Ce nanophosphors prepared with laser ablation.



**Fig. 4.** UV-vis transmission spectra of (a) a bare overhead transparency film, (b) YAG:Ce nanophosphors coated onto an overhead transparency film, and (c) the YAG:Ce target phosphor coated onto an overhead transparency film.

YAG:Ce nanophosphor contain lattice fringes due to (420) planes, as shown in Fig. 3(f). The HRTEM images reveal the highly crystalline nature of the YAG:Ce nanophosphors, and confirm that the crystalline nature of the bulk target YAG:Ce phosphor is not destroyed by the laser ablation process.

The UV-vis spectra shown in Fig. 4 were recorded to compare the optical transparencies of the YAG:Ce target

phosphor and the YAG:Ce nanophosphors. Suspensions in PAS ink of the YAG:Ce target phosphor and the YAG:Ce nanophosphors were coated onto commercial overhead transparency (OHP) films with a thickness of 90  $\mu\text{m}$ . The transmittances at 500 nm of the OHP films coated with YAG:Ce nanophosphors and the YAG:Ce target phosphor are 90% and 82% respectively of that of the bare OHP film. Thus, 44% of the back-scattering effect due to the micron-sized YAG:Ce phosphor can be eliminated by preparing nano-sized phosphors with laser ablation. Since the temperature inside the epoxy capsule of a high power white LED reaches 160°C, the photoluminescence intensity of the YAG:Ce phosphors does not decrease during the operation of a high power white LED.

Figure 5 shows the photoluminescence emission spectra of the YAG:Ce target phosphor and the YAG:Ce nanophosphors prepared with laser ablation at various temperatures in the range 300 K to 420 K. The photoluminescence properties of both the YAG:Ce target phosphor and the YAG:Ce nanophosphors are thermally stable. These results confirm that the photoluminescence properties of the YAG:Ce nanophosphors are not affected by the formation of nanoparticles during laser ablation. Therefore, the YAG:Ce nanophosphors prepared with laser ablation can be used as yellow emitting phosphors in a high power phosphor-converted white LED.

#### 4. CONCLUSIONS

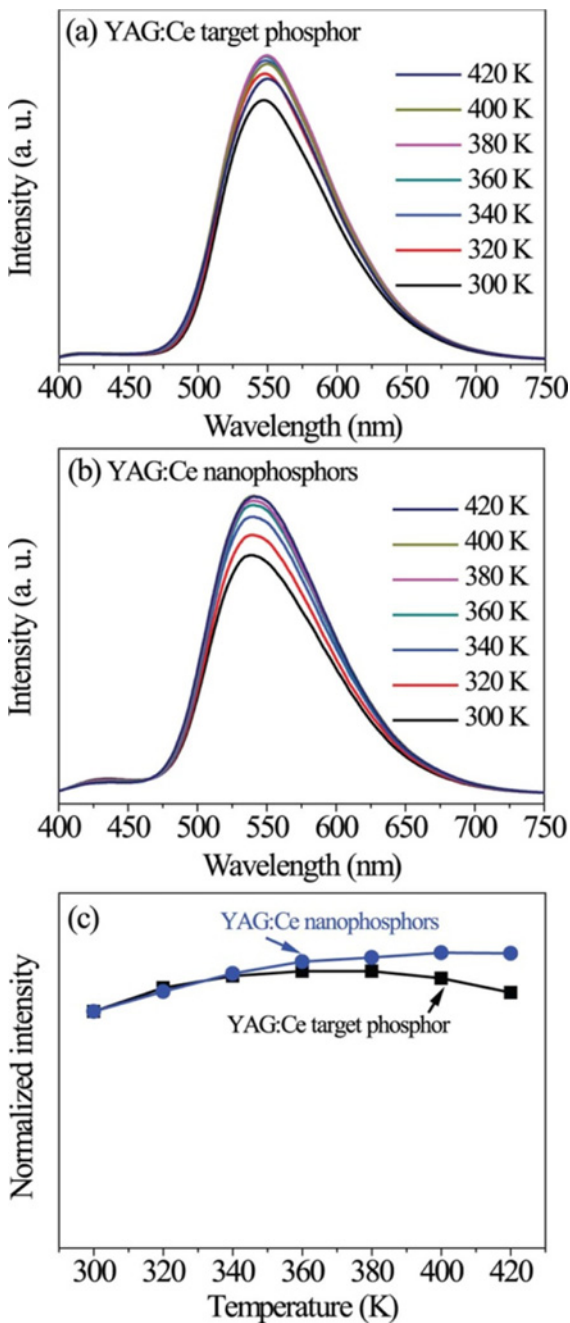
YAG:Ce nanophosphors with a mean size of 15 nm were prepared by performing the laser ablation of a micron-sized commercial YAG:Ce target phosphor. The photoluminescence intensity of the YAG:Ce nanophosphors is almost equal to that of the micron-sized YAG:Ce target phosphor. Surface defects do not form in significant quantities during the laser ablation process. The transmittance of the YAG:Ce nanophosphor is superior to that of the YAG:Ce target phosphor. A large decrease in the back-scattering is obtained due to the formation of nanoparticles. The good thermal stability of the YAG:Ce nanophosphors was also confirmed. The YAG:Ce nanophosphors prepared with laser ablation can be used as excellent yellow emitters in a high power white LED.

#### ACKNOWLEDGEMENTS

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**Fig. 5.** Photoluminescence spectra of (a) the YAG:Ce target phosphor and (b) the YAG:Ce nanophosphors prepared with laser ablation at various temperatures. (c) Relative photoluminescence intensities of the YAG:Ce target phosphor (black line, square) and the YAG:Ce nanophosphors (blue line, circle) with respect to the temperature.

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