TAG:Ce^{3+} Phosphors Prepared by a Novel Sol-combustion Method for Application in InGaN-based White LEDs

Yibo Chen, Jing Wang, Menglian Gong,* Qiang Su, and Jianxin Shi
State Key Laboratory of Optoelectronic Materials and Technologies & School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China

(Received January 10, 2007; CL-070028; E-mail: cesgml@mail.sysu.edu.cn)

$Tb_3Al_5O_{12}$:Ce^{3+} (TAG:Ce^{3+}) phosphors were prepared by a novel sol-combustion (SC) method, and the samples showed improved luminescent properties than those by conventional solid-state (SS) method. Bright white LEDs were fabricated and the performances of the LEDs confirm that TAG:Ce^{3+} prepared by SC method is a good phosphor for white LEDs with low color temperature for indoor lighting.

Recently, semiconductive white light-emitting diodes (WLEDs) have emerged as a novel generation of illumination technology.[1–3] Although the widely applied LEDs are made from YAG:Ce^{3+} phosphor and a blue chip, there still exists a problem that the color temperature of the LEDs was too high (6000–7000 K) to be applied as an indoor warm-lighting because of lack of red light. Terbium aluminum garnet ($Tb_3Al_5O_{12}$, TAG) is a conventional magneto-optical material, but the spectrum of TAG host material with the activator Ce^{3+} is slightly shifted to red range, which is advantageous to resolve the problem of higher color temperature of YAG:Ce^{3+}-LEDs.[4,5] Kummer and Batentschuka et al.[6,7] reported that TAG:Ce^{3+} was a novel phosphor for warm white LED application and prepared it by SS method at 1500 °C. Lately, Chiang and his co-workers reported the preparation of TAG:Ce^{3+} powders by coprecipitation (CP) method and predicted that it would be used to make a "warmer" WLED than YAG:Ce^{3+}.[8] In this letter, the TAG:Ce^{3+} phosphors were made by a novel sol-combustion method; white LEDs were fabricated with the phosphors, and the luminescent properties of the phosphor and the LEDs were studied in details.

It has been found that the critical concentration of Ce^{3+} is 4% for TAG host by SS method at 1500 °C in prophase of our work, so we chose 4% as the doping concentration of Ce^{3+} in the SC method. Firstly, Tb_4O_7 (99.99%) was dissolved in dilute nitric acid; $Ce(NO_3)_3$ (AR) and $Al(NO_3)_3 \cdot 9H_2O$ (99.9%) were dissolved in distilled water. The nitrate solutions were mixed with a molar ratio of 2.88:5.00:0.12 for Tb:Al:Ce, and an appropriate amount of citric acid was added to yield a metal ions/citric acid molar ratio of 1:2. The resultant mixture was stirred at 70–80 °C until a sticky sol was obtained. The sol was dried in an oven at 180–250 °C for a few minutes, and a fluffy precursor remained. The precursor was preheated at 700 °C for 3 h in air and ground, then the powder was sintered at various temperatures from 800 to 1450 °C for more than 10 h in CO atmosphere. Several LEDs were fabricated by combining the obtained TAG:Ce^{3+} phosphors with ca. 460 nm emitting InGaN chips while the commercial YAG:Ce^{3+}-LEDs were also made for comparison. X-ray powder diffraction (XRD) patterns of the products were recorded on a Rigaku D/max - IIIA diffractometer with Cu Kα radiation. The morphology of the samples was inspected using a JEOL JSM-6330F field emission scanning electron microscope (FESEM). Excitation and emission spectra of the powdered phosphors were measured on a Fluorolog-3-21 spectrometer (JOBIN YVON, America) at room temperature. The emission spectra of the LEDs were recorded on a PMS-50 LED spectrophotocolorimeter (EVERFINE, China).

Figure 1 illustrates the X-ray diffraction patterns of TAG:0.04Ce^{3+} calcined at different temperatures. It was found that the patterns were in good consistence with that of the JCPDS #17-35 ($Tb_3Al_5O_{12}$, body-centered cubic) and no $TbAlO_3$ (TAP) peaks emerged as intermediate phase at a temperature of 950 °C or higher. Compared to SS method, the SC method can reduce the phase-formation temperature of TAG by more than 500 °C, which can be attributed to the homogeneous cross-linking of the metal centers and improved reactivity of the precursor. The intensities of the diffraction peaks increased as the calcination temperature increased owing to the enhancement of the crystallinity.

The morphology of the crystalline TAG:0.04Ce^{3+} phosphors prepared by SC method at different temperatures is shown in Figure 2. As the calcination temperature increased, the crystallites grew up, so the particle radii showed an obvious increasing tendency: 50–100 nm at 950 and 1100 °C, 200–300 nm at 1200 °C, submicrometers at 1300 °C and even micrometers at 1400 and 1450 °C. The powders obtained at lower temperatures showed spindle-like morphology while the powders at higher temperatures was anomalous, even though they still showed a more uniform morphology than that of the powders by SS method for which radii always lay in a range of 2–8 μm.

The excitation ($\lambda_{em} = 550$ nm) and emission ($\lambda_{ex} = 463$ nm) spectra of TAG:0.04Ce^{3+} phosphor prepared by SC method at 1450 °C are presented in Figure 3. The broad excitation band centering at ca. 463 nm is attributed to f–d electron transition of Ce^{3+}. Strong and broad green-yellow emission band peaking at ca. 550 nm is found under 463-nm light excitation,

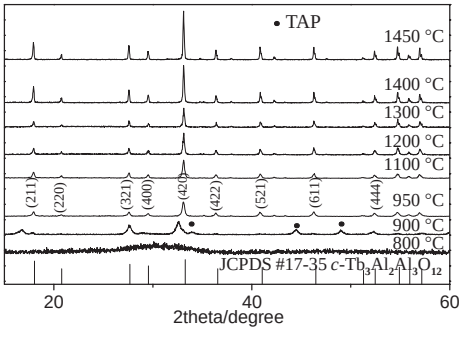

Figure 1. XRD patterns of TAG:0.04Ce^{3+} prepared by SC method at various temperatures.

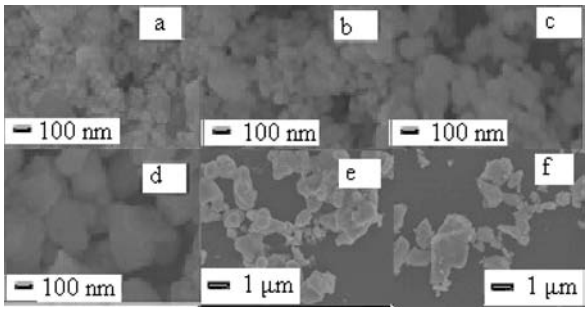

Figure 2. FESEM images of crystalline TAG:0.04Ce^{3+} phosphors prepared by SC method at different temperatures of 950 °C (a), 1100 °C (b), 1200 °C (c), 1300 °C (d), 1400 °C (e), and 1450 °C (f).

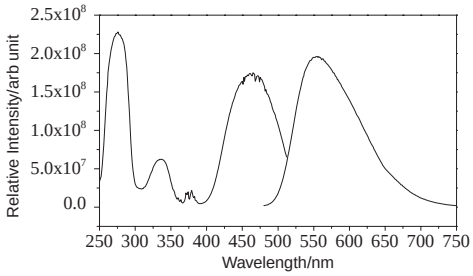

Figure 3. The excitation ($\lambda_{em} = 550$ nm) and emission ($\lambda_{ex} = 463$ nm) spectra of TAG:0.04Ce^{3+} phosphor prepared by SC method at 1450 °C.

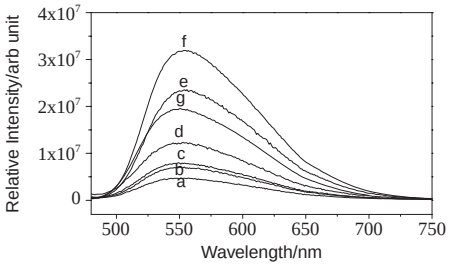

Figure 4. The emission spectra of TAG:0.04Ce^{3+} phosphors prepared by SC method at different temperatures of 950 °C (a), 1100 °C (b), 1200 °C (c), 1300 °C (d), 1400 °C (e), 1450 °C (f), and by SS method at 1500 °C (g) ($\lambda_{ex} = 463$ nm).

which is matched with the emission wavelength of a blue-emitting InGaN chip and reveals that the phosphor is a good candidate for fabrication of InGaN-based LEDs.

The comparison of the relative emission intensities of the TAG:0.04Ce^{3+} phosphors prepared by the SC method with those of the sample prepared by SS method is shown in Figure 4. It was found that the emission intensities of the TAG:0.04Ce^{3+} phosphors prepared by SC method increased along with the increase of calcination temperature. XRD measurement indicates the enhancement of the crystallinity when the calcination temperature increases, and higher crystallinity leads to enhanced emission. More importantly, when the calcination temperature rose to above 1400 °C, the emission intensities of the phosphors were even higher than those of the sample made by SS method at 1500 °C. The emission enhancement for the SC samples depends on the characteristics of the sol-combustion method. Firstly, it is upgradeed compared to Pechini method.[9,10] In the SC process,

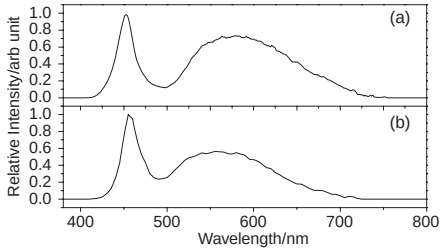

Figure 5. The emission spectra of the LEDs made from TAG:0.04Ce^{3+} phosphors prepared by the SC method (a) and commercial YAG:Ce^{3+} phosphors (b).

the combustion occurring at 180–250 °C produces a very fluffy precursor, and it is beneficial to complete burning off of the organic compounds in the following step. Secondly, the citric acid as a chelate ligand can prevent the hydrolysis of the metal cations, so that a homogeneous distribution of activators can be realized and it leads to higher emission compared to that of SS method, in which the starting materials cannot be mixed completely. Thus, the SC method is confirmed to be an easy and effective process for preparation of highly efficient TAG:Ce^{3+} phosphors.

The emission spectra of the LEDs under 20-mA forward bias are shown in Figure 5. Bright light emission produced both from TAG:Ce^{3+}-LED and YAG:Ce^{3+}-LED is located inside the white light domain in the CIE diagram with the CIE chromaticity coordinates of (0.3748, 0.3521) and (0.3235, 0.3513), respectively. However, the color temperature of the TAG:Ce^{3+}-LED is 3952 K, much lower than that of the YAG:Ce^{3+}-LED (5877 K) while their color rendering indexes are similar (75.8 and 76.6, respectively). The performance of the TAG:0.04Ce^{3+}-LED prepared by the SC method indicates that it is a good phosphor for fabrication of white LEDs with lower color temperature for indoor lighting.

In conclusion, TAG:Ce^{3+} phosphors were prepared by a novel SC method. Strong emissions centering at ca. 550 nm can be obtained by exciting the TAG:Ce^{3+} phosphors with 463-nm light. SC method is an easy and effective method for preparing highly efficient TAG:Ce^{3+} phosphors. The good performance of the TAG:0.04Ce^{3+}-LED confirms that TAG:Ce^{3+} prepared by the SC method is a good phosphor for fabrication of white LEDs with lower color temperature for indoor lighting.

This work was funded by research grants from the Guangdong Province Government (Grant No. ZB2003A07) and from the Scientific and Technical Projects of Guangzhou City Government (Grant No. 2005Z2-D0061).

References

1 J. H. Yum, S.-Y. Seo, S. Lee, Y.-E. Sung, *J. Electron. Soc.* **2003**, *150*, H47.
2 J. S. Kim, P. E. Jeon, Y. H. Park, J. C. Chol, H. L. Park, G. C. Kim, T. W. Kim, *Appl. Phys. Lett.* **2004**, *85*, 3696.
3 J. K. Park, C. H. Kim, S. H. Park, H. D. Park, S. Y. Chol, *Appl. Phys. Lett.* **2004**, *84*, 1647.
4 L. Mu-jen, U. S. Patent 20050161690, **2005**.
5 A. Ellens, Int. Pat. Appl. WO2001093342, **2001**.
6 F. Kummer, Int. Pat. Appl. WO2001008452, **2001**.
7 M. Batentschuk, A. Osvet, G. Schierning, A. Klier, J. Schneider, A. Winnacker, *Radiat. Meas.* **2004**, *38*, 539.
8 C. C. Chiang, M. S. Tsai, M. H. Hon, *J. Alloys Compd.* **2007**, *431*, 298.
9 M. P. Pechini, U. S. Patent 3330697, **1967**.
10 C. A. Kodaira, H. F. Brito, M. C. Felinto, *J. Solid State Chem.* **2003**, *171*, 401.

Published on the web (Advance View) May 19, 2007; doi:10.1246/cl.2007.760