

An efficient nitridation approach to enhance luminescent intensity of YAG : Ce³⁺ phosphor by using hexamethylenetetramine

Pin-Chun Lin^a, Chien-Hao Huang^b and Wei-Ren Liu^{a,*}

^aDepartment of Chemical Engineering, Chung Yuan Christian University, Taiwan

^bMaterial and Chemical Research Laboratories, Industrial Technology Research Institute

Nitrogen-doped YAG : Ce³⁺ phosphors have been firstly studied by using hexamethylenetetramine (HMT) as a nitrogen source by a solid state reaction. The optimal content of HMT is by introducing 50 wt.% with precursors of Y₂O₃, Al₂O₃ and CeO₂ under annealing at 1450 °C for 8 hours. The XRD data indicate that the lattice constants increase with the content of HMT. SEM morphologies demonstrate that after nitrogen doping, the surface and particle size of YAG become smoother and larger than un-treated one. The PL intensity of YAG : Ce after HMT treatment gives a incensement in range of 3.46% ~ 9.87%. The luminous efficacy of as-synthesized YAG : Ce phosphor + Blue chip was dramatically enhanced by 40%. Using the doped samples, the white LED luminous efficiency obtained 78.4 lm/W and was successfully obtained with the combination of blue LED chip, thus improving the performance of the LED. The enhancement in luminesce was resulted from the modification of its surface morphology, crystallinity and grain size.

Key words: Hexamethylenetetramine, Nitrogen, Light emitting diodes, Phosphors.

Introduction

Light converting inorganic luminesce materials in conjunction with light emitting diodes (LEDs) have attracted great attentions in recent years due to the merits of high energy efficiency, long lifetime, and low-power consumption [1-2]. From the view point of cost issue, the generation of white light, in general, is by using blue-emitting InGaN chips and yellow-emitting phosphors. Nowadays, commercially available yellow emitting phosphors includes (Ba,Sr,Ca)₂SiO₄ : Eu²⁺, Ca- α -SiAlON:Eu²⁺, Y₃Al₅O₁₂ : Ce³⁺, LaSi₃N₅ : Ce³⁺ and so on. Among these yellow phosphors, Y₃Al₅O₁₂ : Ce³⁺ phosphors (YAG : Ce) have been wide used because of their low cost, high quantum efficiency, good thermal quenching and excellent chemical stability.

In order to enhance the lumen efficacy and color rendering index of LED devices, much efforts have been devoted for improving the luminesce properties of YAG : Ce [3-9] by means of fluxes, synthetic methodologies, precursors, sintering process and so on. Lakshmanan *et al.* [3] investigated the flux effects on the photoluminescence efficiency of YAG : Ce. This study mentioned that suitable fluxes could enhance stability and high luminous intensity of YAG : Ce³⁺ phosphors. Lin *et al.* [4] increased the luminous intensity of YAG : Ce phosphors by ~ 22.7% via adding H₃BO₃ and BaF₂ as fluxes during sintering process [4].

Shiqing *et al.* [5] discussed the relationship between different fluxes and the luminous intensity for optimizing the phosphor-preparation processes. Won *et al.* [6] also successfully improved the luminous intensity of phosphor by flux technique. Apart from the addition of fluxes, particle size control is also important issue in improving the luminous intensity of the phosphor. Huan *et al.* [7] studied the effect of the particle size of YAG phosphor on the luminous intensity of LED devices. Liu *et al.* [8] scrutinized the effects of the particle size of YAG : Ce³⁺ phosphor on the performance of LED devices. Another method to increase the luminous intensity was studied by Tsai *et al.* in 2007 by changing the conditions of the synthesis of the phosphor [9].

To the best of our knowledge, there has been no study on the luminescent properties of YAG : Ce³⁺ by using hexamethylenetetramine as a nitrogen source to enhance its luminesce, surface morphology and crystallinity. The characterizations of w/wo HMT-treated YAG samples will be carried out by XRD, SEM, EDX as well as PL and LED package in this study.

Experimental Procedures

X-ray diffraction (XRD) patterns were recorded with Cu K α radiation ($\lambda = 0.154$ nm) generated at 45 kV/ 40 mA. They were collected in the 2θ range of 10-80 ° with a scan speed of 5 °/min. The PL emission spectra of polycrystalline YAG : Ce³⁺ phosphors were characterized via fluorescence spectrophotometer (F-4500, FL Spectrophotometer, wavelength range: 480-800 nm, scan speed:

*Corresponding author:
Tel : +886-3-265-4140
Fax: +886-3-265-4199
E-mail: WRLiu1203@gmail.com

1200 nm/min, excitation slit: 5 nm, emission slit: 5 nm, PMT voltage: 400 V) with a 150 W Xenon short-arc lamp as an excitation source (Ushio, Tokyo, Japan). Micrographs of as-received samples were observed by scanning electron microscopy (SEM, JEOL, JSM-7600F) under a working voltage of 20 kV. Element analysis was carried out by EDS (Oxford, Xmax80 1.).

The powder samples of $Y_3Al_5O_{12-x}N_x : Ce^{3+}$ were prepared by a conventional solid state reaction. The starting materials were Y_2O_3 (purity: 99.9%, Aldrich), Al_2O_3 (purity: 99.9%, Aldrich), CeO_2 (purity: 99.998%, Strem), and mixed thoroughly along with a certain amount of H_3BO_3 (purity: 99.9995%, Strem) and BaF_2 (purity: 99.9%, Aldrich) as fluxes. Doped with different weight percent of $C_6H_{12}N_4$ (purity: 9.99%, Aldrich). All starting materials were weighed according to stoichiometric ratio. After the starting materials had been mixed sufficiently, they were sintered at 1450 °C for 8 hours under a reductive atmosphere (15% H_2 /85% N_2).

Results and Discussion

In this study, we use hexamethylenetetramine (HMT) as a doping source of nitrogen during synthetic process of YAG : Ce via a solid state reaction. HMT is a white powder with a chemical formula of $C_6H_{12}N_4$. The

density and melting point are 1.33 g/cm³ and 280 °C, respectively. White heating the sample high than 280 °C, $C_6H_{12}N_4$ would decompose into CO_2 , H_2O and NH_3 . Owing to the lower melting point and the presence of ammonia at higher temperature, HMT might be good candidates as not only a flux but also a doping source of nitrogen in the phosphor synthetic process. The XRD patterns of YAG : Ce with different weight percent of HMT are shown in Fig. 1. The XRD pattern demonstrate no any crystalline impurity in these samples. Fig. 1(b) shows the characteristic diffraction peak in larger magnitude. Obviously, with increasing the amount of HMT after sintering process, the characteristic peak of $\sim 33.43^\circ$ shift to 33.39° , which was resulted from the lattice expansion of YAG lattice.

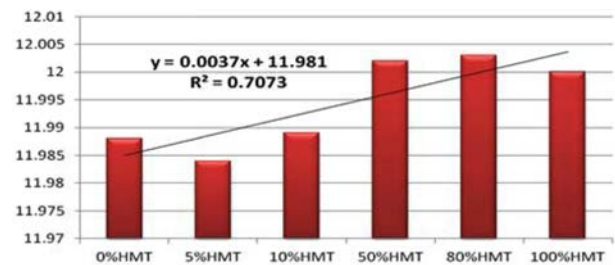


Fig. 2. Lattice constant of HMT with different content of HMT after sintering process.

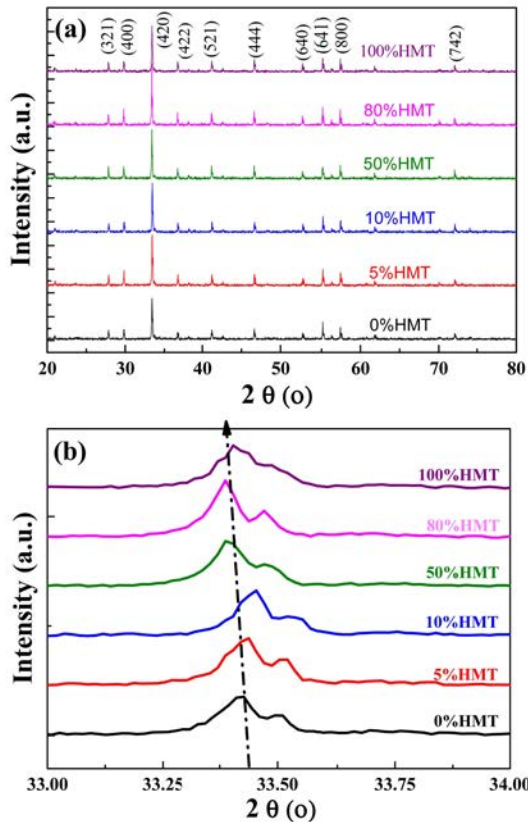


Fig. 1. (a) XRD patterns of YAG : Ce phosphors with different content of HMT after sintering at 1450 °C; (b) XRD magnified part patterns of YAG : Ce phosphors with different contents of HMT.

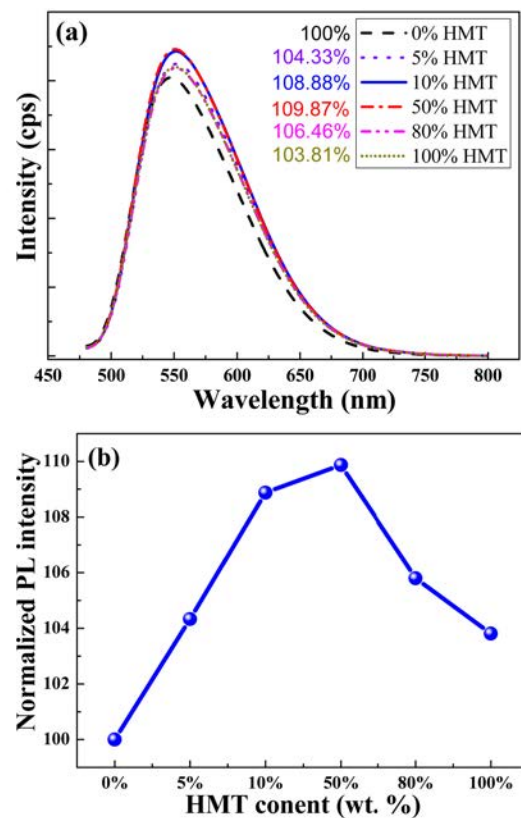


Fig. 3. (a) PL Emission spectra of YAG : Ce phosphors under excitation of 460 nm with different content of HMT at 1450 °C; (b) Normalized photoluminescence intensity with different content of YAG : Ce.

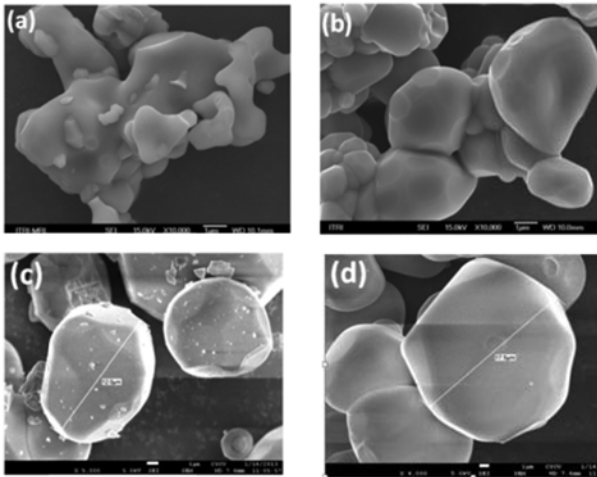
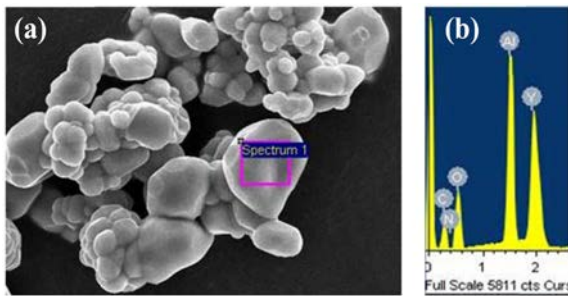


Fig. 4. SEM images of (a) YAG : Ce; (b) YAG : Ce with 80 wt.% HMT; (c) Commercial YAG : Ce; (d) Commercial YAG : Ce with 10 wt.% HMT.



(c) Elements	Weight%	Atomic%
N	4.79	9.44
O	33.30	57.51
Al	19.38	19.51
Y	42.46	13.21
Total	100.00	100.00

Fig. 5. YAG : Ce with 80 wt.% HMT: (a) SEM image; (b) and (c) EDS analysis.

By introducing 80 wt.% of HMT into precursors with sintering process, N-doped YAG : Ce exhibits the larger lattice constants. The lattice expansion of YAG lattice might be due to the fact of oxygen atoms were replaced by nitrogen atoms during the nitridation process. Fig. 2 display the lattice constant as a function of HMT contents. The result indicates that the lattice constant increase with the content of HMT with a linear relationship.

Fig. 3(a) displays the emission spectra of YAG : Ce doped with varying amount of HMT sintered at 1450 °C with excitation wavelength of 460 nm. The PL spectra showed that 50 wt.% HMT exhibits the highest intensity, which is 9.87% than that of bare YAG : Ce phosphors. More HMT content, however, gives a

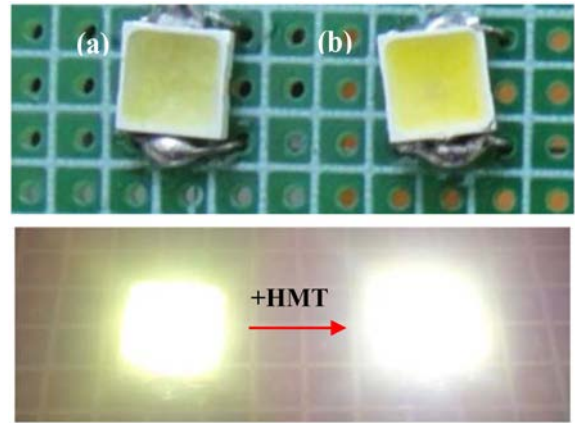


Fig. 6. Package appearance of (a) YAG : Ce and (b) YAG : Ce with 50 wt.% HMT.

Table 1. PL intensity of YAG : Ce and luminous efficacy of LED.

Samples	PL intensity	Luminous efficacy (lm/W)
YAG : Ce	100	54.3
Precursor + 50HMT	100.87	78.4

slight decrease of luminescence, which might be due to the etching effect resulted from much ammonia concentration in the furnace. The optimal content of HMT is 50 wt.%.

Fig. 4 show the surface morphologies of (a) YAG : Ce, (b) YAG : Ce with 80 wt.% HMT, (c) commercial YAG : Ce and (d) commercial YAG : Ce sintering with 10 wt.% HMT, respectively. The morphologies of YAG : Ce doped after HMT treatment become much smoother and granular compared with the un-treated those. The result indicates that HMT might also play a role of flux also during sintering process due to its nature of lower melting point. Thus, the crystalline of YAG : Ce phosphor could also be improved by HMT treatment for both precursors or commercial YAG phosphors.

Fig. 5 (a-c) shows the SEM image and EDS analyses of YAG : Ce phosphor with 80 wt.% HMT treatment. The nitrogen content was measure to be 9.44 mol.% after 80% HMT treatment. The result future confirm that nitrogen was indeed into the lattice.

The fabrication of blue LED chip with un-doped YAG : Ce or N-doped YAG : Ce phosphors is also carried out and shown in Fig. 6. The PL intensity of YAG : Ce powder and its corresponding efficiencies of the packaged LEDs with or without HMT treatment are displayed in Table 1. The N-doped YAG : Ce phosphor exhibits higher luminous efficiency compared to the un-doped by 40%. The results demonstrate that doping nitrogen into YAG : Ce with HMT could dramatically enhance the luminous efficiency.

Conclusions

In this study, we report an efficiency nitridation technology of YAG:Ce phosphors via introducing nitrogen-containing compound, said HMT, in conjunction with subsequent sintering to obtain nitrogen-doped YAG phosphor with highly crystallinity. The emission intensity of the as-synthesized YAG phosphor could be dramatically enhanced by 9% compared to un-treated sample. The SEM and EDS data further proved that the presence of nitrogen in the YAG:Ce host lattice improved the luminescence and the surface morphology by enhancing the smoothness of the surface and the crystallinity of the phosphor. Also, in the packaged LED, HMT doped YAG:Ce revealed better luminescence efficiency compared to the un-doped YAG:Ce. Thus, it is a good method to nitride YAG:Ce to obtain better luminous intensity and efficacy.

References

1. S. Ye, F. Xiao, Y. X. Pan, Y. Y. Ma and Q. Y. Zhang, *Mat. Sci. Eng. R.* 71 (2010) 1-34.
2. W. B. Im, Y. I. Kim, N. N. Fellows, H. Masui, G. A. Hirata, S. P. DenBaars, and R. Seshadri, *Appl. Phys. Lett.* 93 (2008) 091905-091905-3.
3. A. Lakshmanan, R. S. Kumar, V. Sivakumar, P. C. Thomas, and M. T. Jose, *Indian J. Pure Ap. Phys.* 49 (2011) 303-307.
4. Y. S. Lin and R. S. Liu, *J. Lumin.* 580 (2007) 122-123.
5. X. U. Shiqing, S. N. Liuzheng, Z. Ying, J. U. Haidong, Z. A. Shilong, D. G. Degang, H. P. Wang and B. L. Wang, *J. Rare Earth.* 27 [2] (2009) 327-329.
6. C. W. Won, H. H. Nersisyan, H. I. Won, J. H. Lee and K. H. Lee, *J. Alloys Compd.* 509 (2011) 2621-2626.
7. S. C. Huang, J. K. Wu, W. J. Hsu, S. C. Huang, J. K. Wu, W. J. Hsu, H. Y. Su, N. Bagkar, W. C. Ke, H. T. Kuo and R. S. Liu, *Int. J. Appl. Ceram. Tech.* (2009) 465-469.
8. Z. Y. Liu, C. Le, B. H. Yu, Y. H. Wang, S. Liu and H. B. Niu, *J. Display Technol.* 8 (2011) 329-335.
9. M. S. Tsai, W. C. Fu and G. M. Liu, *Journal of Alloys and Compounds* 440 (2007) 309-314.