

Spectral Properties of Various $Y_3Al_5O_{12}:Ce^{3+}$ Nanocrystalline Phosphors for the Application of White LEDs

Heesun Yang^{1,*}, Mi-Jung Jeon¹ and Young-Duk Huh²

¹Dept. of Materials Science and Engineering, Hongik University, Seoul Korea

TEL:82-2-320-3039, e-mail: hyang@hongik.ac.kr

²Dept. of Chemistry, Dankook University, Seoul Korea

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Abstract

Various yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) nanocrystalline phosphors, where some Al^{3+} sites are substituted with Ga^{3+} or some Y sites with Gd^{3+} , have been synthesized. The rare earth ions such as Pr^{3+} and Tb^{3+} were also co-doped into YAG:Ce system, leading to the tunability of CIE coordinates of emission.

1. Introduction

For recent years, white light emitting diodes (LEDs) have been used as an LCD backlight source as well as an illumination light source. A combination of a blue LED and a yellow phosphor is commonly used due to its low fabrication cost compared to the white LED mixed with red, green, and blue LEDs [1]. To be used as a backlight source, white LEDs should have a wide range of color gamut. However, a yellow-emitting YAG:Ce phosphor-based white LED has a limited color gamut of 70% of National Television Standards Committee (NTSC). In our study, various YAG:Ce nanocrystalline phosphors with different chemical compositions are synthesized via a soft chemistry, and their spectral properties are tuned ultimately for the improvement of the color gamut of white LEDs.

2. Experimental

In a typical synthesis of Ce-doped YAG nanocrystalline phosphors, Al nitrate, Y nitrate, and Ce nitrate were used and mixed with water, polyvinylpyrrolidone (PVP, $M_w=1000$) and citric acid. For the modified composition of YAG:Ce, all nitrate form of Ga^{3+} , Gd^{3+} , Pr^{3+} , and Tb^{3+} was used. The reaction of the mixture at 80°C for 2hr was maintained, and reactants were further heated at 160°C for 12hr. The as-synthesized nanocrystalline powders were post-annealed at 1000, 1200, and 1400°C for 6hr in an

air atmosphere. The X-ray diffraction (XRD), scanning electron microscopy (SEM), and spectrofluorometer were utilized for the characterization of crystal structure, morphology, and optical properties, respectively, of annealed samples.

3. Results and discussion

Fig. 1(a) shows XRD patterns of YAG:Ce (0.06 mol% of Ce concentration) samples as a function of annealing temperature. The SEM image of 1200°C-annealed sample is also shown in Fig. 1(b). As-

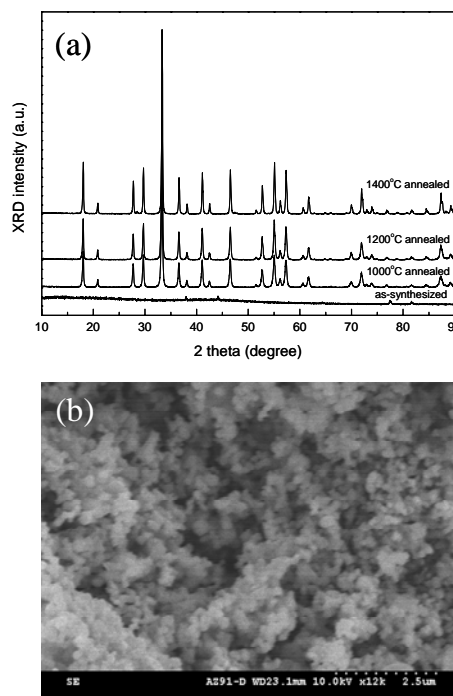


Fig. 1. (a) XRD patterns of YAG:Ce as a function of annealing temperature and (b) SEM image of 1200°C-annealed YAG:Ce nanocrystalline.

synthesized sample did not show any characteristic XRD peaks, indicating an amorphous phase. Annealed samples showed a typical cubic structure of YAG [1,2] and their full-width-at-half-maximum (FWHM) became narrower with a higher annealing temperature. The average size of about 200nm was observed in 1200°C-annealed nanocrystalline YAG:Ce in Fig. 1(b).

As shown in Fig. 2(a), the Ce³⁺-related PL (photoluminescence) emission at 528nm became stronger with a higher annealing temperature due to a better crystallinity. Therefore all samples were post-annealed at 1400°C for 6hr in air. The Ce³⁺ emission is involved with the ground 4f¹ configuration and the excited 4f⁰5d¹ state. The 4f¹ and 4f⁰5d¹ state are split into ²F_{7/2}, ²F_{5/2} and ²D_{3/2}, ²D_{5/2} states, respectively, due to the spin-orbital coupling [1-3]. The Ce³⁺ emission results from the electron transition from the lowest 5d band to ²F_{7/2}, ²F_{5/2} states of the Ce³⁺ ion. Fig. 2(b) shows the typical PL excitation spectrum of 1400°C-annealed sample. Two excitation bands are involved with the electronic transitions from the ground state of Ce³⁺ (²F_{5/2}) to the different crystal field splitting bands of excited 5d state of Ce³⁺ ion.

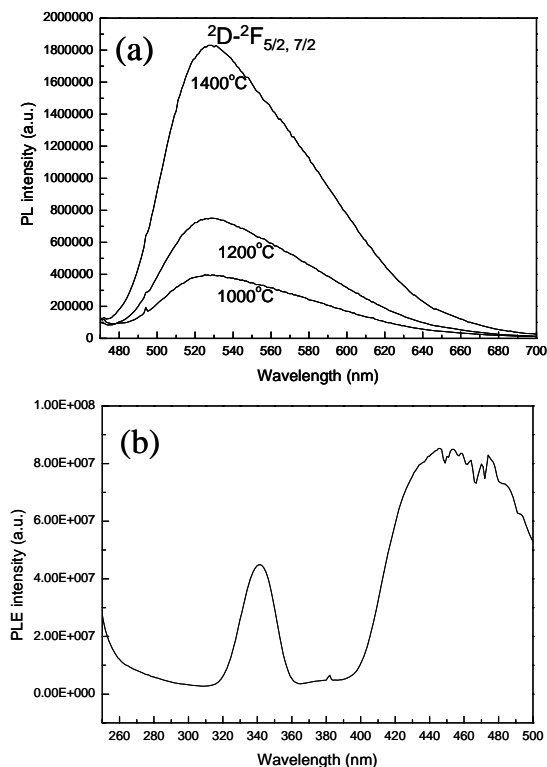


Fig. 2. (a) PL emission spectra of YAG:Ce samples as a function of annealing temperature (excitation wavelength of 440nm) and (b) PLE spectrum of 1400°C-annealed sample (detected wavelength of 520nm).

The Ce³⁺ emission in a YAG host can be tuned by substituting Y site or Al site with different types of cation [4,5]. The spectral emission of YAG:Ce was blue-shifted by substituting some of Al³⁺ sites with larger size of Ga³⁺ ion due to the smaller crystal splitting. The spectral variation of Y₃Al_{5-x}Ga_xO₁₂:Ce is shown in Fig. 3(a), indicating a gradual blue-shift of Ce emission from 525 (for x=0.25) to 518 nm (for x=1.0). The opposite spectral trend is observed in Fig. 3(b), where some Y sites in a YAG host are substituted with larger size of Gd³⁺ ions. The Ce emission in Y_{3-x}Gd_xAl₅O₁₂:Ce was red-shifted from 532 (for x=0.25) to 545 nm (for x=1.0).

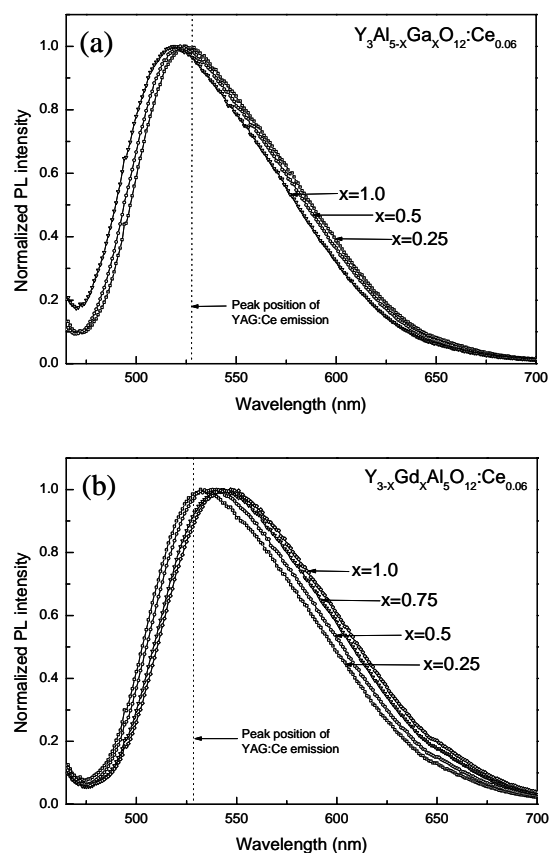


Fig. 3. A series of PL emission spectra of (a) Ga-substituted and (b) Gd-substituted YAG:Ce nanocrystalline phosphors (excitation wavelength of 440nm).

The alternative emission tunability can be realized by incorporating co-activators such as red-emitting Pr³⁺ or green emitting Tb³⁺ into a YAG:Ce system. To add a red emission component into a yellow-YAG:Ce nanocrystalline phosphor, 0.006 mol of Pr³⁺ ion was

co-doped, and PL emission and excitation spectra are shown in Fig. 4(a) and (b), respectively. When excited by a blue light of 440nm, YAG:Ce_{0.06}Pr_{0.006} nanocrystalline phosphor exhibited a typical Ce emission which is well overlapped with red emission lines. Particularly, the red emission component at 610nm is involved with the characteristic Pr³⁺ transition of ¹D₂-³H₄ [1]. Since a 440nm does not contribute to the direct electronic excitation of Pr³⁺ ion, the appearance of 610nm-red line emission results from the energy transfer from the excited Ce³⁺ to co-existing Pr³⁺ ion. The excitation energy may be transferred from the lowest 5d band of Ce³⁺ to ¹D₂ state of Pr³⁺ by a radiative pathway. The PLE spectrum (detected emission wavelength of 520nm) in Fig. 4(b) consists of three excitation bands, i.e., the first band at 287nm corresponding to Pr³⁺-related excitation (4f²-4f5d) and the rest two bands to Ce³⁺ excitation bands, whereas no Ce³⁺-related excitation band at 287nm is observed for YAG:Ce sample as shown in Fig. 2(b). Therefore, it is believed that reverse energy transfer from the excited 4f5d state of

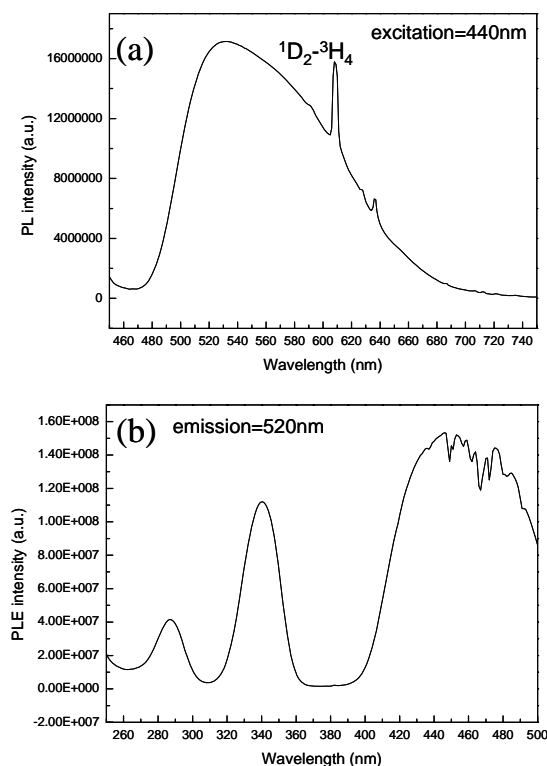


Fig. 4. (a) PL emission spectrum and (b) PLE spectrum of YAG:Ce_{0.06}Pr_{0.006} nanocrystalline phosphor.

Pr³⁺ to Ce³⁺ ion can occur presumably by a radiative or non-radiative pathway.

In addition to YAG:Ce,Pr nanocrystalline phosphor, the Tb³⁺ ion was used as a green emitting component. The PL emission and excitation of YAG:Ce_{0.06}Tb_{0.1} nanocrystalline phosphor are shown in Fig. 5(a) and (b), respectively. When excited with UV light of 273nm, YAG:Ce_{0.06}Tb_{0.1} nanocrystalline phosphor shows the characteristic Tb³⁺ peaks due to ⁵D₄-⁷F₅ (542nm lines), ⁵D₄-⁷F₆ (489nm lines), and ⁵D₄-⁷F₄ (585nm lines) transitions as well as Ce³⁺ emission peak [6,7]. Because the Ce³⁺ emission in YAG:Ce can not be excited by 273nm, it is evident that the energy of excited Tb³⁺ ion is transferred to Ce³⁺ ion. The PLE spectrum in Fig. 5(b), where the excitation spectrum (detected emission wavelength of 520nm) contains 4f⁸-4f⁷5d transition band at 273nm due to Tb³⁺ ion and rest two bands due to Ce³⁺ ion, further provides the energy transfer between Tb³⁺→Ce³⁺. The pathway for transferring excitation energy from Tb³⁺ to Ce³⁺ is currently under investigation.

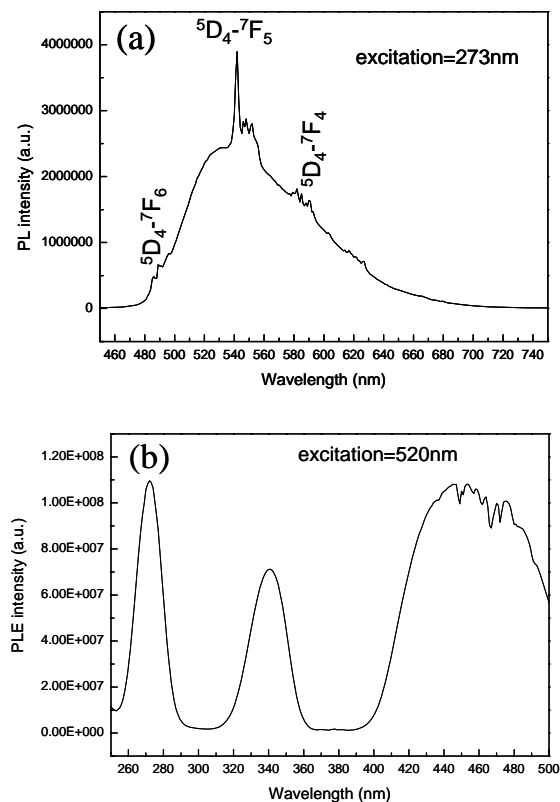


Fig. 5. (a) PL emission spectrum and (b) PLE spectrum of YAG:Ce_{0.06}Tb_{0.1} nanocrystalline phosphor.

4. Summary

The spectral variations of yellow-emitting $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ nanocrystalline phosphors were realized by substituting some Al^{3+} or Y^{3+} sites with larger size of Ga^{3+} or Gd^{3+} ions, leading to blue- or red-shifted emission, respectively. The co-activators such as Pr^{3+} and Tb^{3+} were also incorporated into YAG:Ce system to combine red and green emission components with yellow emission. The respective YAG:Ce,Pr and YAG:Ce,Tb nanocrystalline systems exhibited successful dual emissions with a single excitation wavelength due to the $\text{Ce}^{3+} \rightarrow \text{Pr}^{3+}$ and $\text{Tb}^{3+} \rightarrow \text{Ce}^{3+}$ energy transfer, which can lead to the tunability of CIE coordinates of emission.

5. References

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