PAPER

Correlation between structure and optical properties in $(Y,Lu)_3Al_5O_{12}$:Ce³⁺ solid solutions

To cite this article: Mei Zhang et al 2016 J. Phys. D: Appl. Phys. 49 415101

View the article online for updates and enhancements.

You may also like

- Luminescence Comparison and Enhancement of Ce-doped Yttrium Aluminum Garnet Phosphor via Cation Substitution and Adding Flux Meriel C. Maniquiz, Kyeong Youl Jung and Sang Mun Jeong
- <u>Novel Radiation Device for Application in</u> <u>the UV-A and UV-B Range</u> Michael Laube, Benjamin Herden, Egon Seelbach et al.
- <u>Scattering referenced aerosol phosphor</u> <u>thermometry</u> Dustin Witkowski and David A Rothamer





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 18.118.30.253 on 05/05/2024 at 20:41

J. Phys. D: Appl. Phys. 49 (2016) 415101 (7pp)

Correlation between structure and optical properties in (Y,Lu)₃Al₅O₁₂:Ce³⁺ solid solutions

Mei Zhang¹, Bowen Li¹, Yingshu Yang¹, Shuijin Chen¹, Xin He¹, Fenghua Zhao² and Qingguang Zeng¹

¹ School of Applied Physics and Materials, Wuyi University, Jiangmen 529020, People's Republic of China

² School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, People's Republic of China

E-mail: zmjenny@163.com (M Zhang)

Received 28 May 2016, revised 12 July 2016 Accepted for publication 22 August 2016 Published 14 September 2016

Abstract

A series of $(Y,Lu)_3Al_5O_{12}$: Ce^{3+} (YLuAG:Ce) solid solutions were synthesized via the solid-state reaction route. The phosphors are all of the cubic garnet crystal structures confirmed by x-ray diffraction (XRD). The internal quantum efficiency and emission intensity of the phosphors can be enhanced by increasing the Lu³⁺ content in the host lattice, along with a blue shift of the emission peak. In addition, the blue shift of the emission peak correlates very well with the lattice contraction. Intense light-emitting diodes (LEDs) are successfully fabricated based on the YLuAG:Ce phosphors and 450 nm blue Ga(In)N chips. The luminous efficiency of YLuAG:Ce phosphors converted LEDs increases with elevating Lu³⁺ concentration. The results indicate that Ce³⁺ doped YLuAG solid solutions, especially LuAG:Ce phosphor for solid-state lighting.

Keywords: phosphors, aluminum garnet, light-emitting diodes, solid solutions

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, white light-emitting diodes (LEDs) have been regarded as the most promising light source, which are widely used in the general illumination field. In comparison with conventional lighting technologies such as fluorescent lamps, white LEDs have advantages of low-energy consumption, high efficiency, long lifetime, mercury-free etc [1–4]. The commercial and most potential methods in the solid state lighting are phosphors converted LEDs (pc-LEDs). The current commercial white pc-LEDs are combined with blue Ga(In)N LED (420–480 nm) and the $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) phosphor [5–7]. White pc-LEDs realized by this method have high efficiency. However, due to the lack of red components in the emission spectra of the YAG:Ce phosphor, the pc-LED have a low color rendering index (*Ra*) and high correlated color

temperature (Tc), which can not meet the requirements of some special illumination fields.

Consequently, it is very emergency to improve the luminescent characteristics of the YAG:Ce phosphor. A practical method is to induce a red shift through the modifications of the chemical composition. There have been many literatures to report the red shift of the YAG:Ce luminescence by the substitution of Y^{3+} in the host lattice with Gd^{3+} or other larger trivalent ions [8–10]. Another optional method is to co-dope ions which can show red emission, such as Eu^{3+} , Pr^{3+} and Mn^{2+} [11–13]. The substitution of Al–O for Si–N chemical bonds can also result in a red shift in the emission spectrum of Ce³⁺ ions in YAG host [14, 15]. However, all of the above methods cause the decrease in the quantum efficiency of Ce³⁺, while the shift of Ce³⁺ emission is relatively limited.



Therefore, another choice to obtain the white LED with a high Ra and high luminous efficiency is to pump the red and green phosphors by blue LEDs. Green phosphors can also be obtained from the Ce³⁺ doped YAG materials by substitution of Al^{3+} with Ga^{3+} [16, 17]. However, Ga^{3+} ions can be easily reduced to gallium metals under a reductive atmosphere and influence the optical properties of phosphors. Lu₃Al₅O₁₂:Ce³⁺ used to be as a scintillator, and researchers find that (Y,Lu)₃Al₅O₁₂:Ce³⁺ (YLuAG:Ce) solid solutions can emit tunable color by varying Lu^{3+} and Ce^{3+} content [18–20]. Zhang et al reported the combinatorial optimization of greenyellow emitting $(Y_x Lu_{1-x-y})_3 Al_5 O_{12} : y Ce^{3+}$ (x = 0.1–0.9, y = 0-0.09) phosphors for ceramic scintillators [19]. Shao et al found that the LuAG:Ce phosphors have a blue-shift emission with an improved thermal quenching behavior compared with pure YAG:Ce phosphor [20]. To the best of our knowledge, there are few systematical researches on the correlation between the structure and luminescent proprieties about YLuAG:Ce phosphors.

In the present work, we synthesized a series of YLuAG:Ce phosphors by modifying the chemical compositions. It is aim to realize the enhancive and tunable emission color of Ce^{3+} ions in the YLuAG:Ce solid solutions. Moreover, the correlation of crystal structure and luminescence properties of these materials with different Lu³⁺ and Ce³⁺ concentration are studied systematically. Furthermore, we discuss the corresponding electroluminescent properties of pc-LEDs for the application.

2. Experimental section

2.1. Synthesis

A series of $Y_{3-x-y}Lu_xAl_5O_{12}$: yCe^{3+} (x = 0-2.94, y = 0-0.075) phosphors were prepared by a conventional solid-state reaction under a N₂/H₂ reductive atmosphere. The starting materials were Al₂O₃ (99.9%), Y₂O₃ (99.99%), CeO₂ (99.99%), Lu₂O₃ (99.99%) and AlF₃ (99.9%, flux), respectively. The stoichiometrical mixtures of these materials were wet mixed homogeneously in agate-mortars with ethanol. The mixtures were dried and slowly heated to 1300–1500 °C for 3–6h in a reductive atmosphere (H₂/N₂). Then the samples were cooled down to room temperature. Working in a reductive atmosphere and being doped to a trivalent lattice site, cerium will be built into the host lattice as Ce³⁺. After being ground, the samples were washed with diluted HCl solutions to remove the impurities. Finally, the phosphors were obtained and characterized.

2.2. LEDs fabrication

LEDs were fabricated by using series of $Y_{3-x-y}Lu_xAl_5O_{12}$: yCe^{3+} (x = 0-2.94, y = 0-0.075) phosphors and 450 nm Ga(In)N chips. 0.20 g of the synthesized phosphors were used to be blended with 1 g of the transparent silicones. The mixed materials were precoated on 450 nm chips, and then they were dried in the oven at 140–180 °C and maintained at that temperature for 1 h. Finally, the phosphor-converted LEDs (pc-LEDs) were obtained.

2.3. Characterization

The x-ray diffraction (XRD) patterns of $Y_{3-x-y}Lu_xAl_5O_{12}$: yCe^{3+} (x = 0–2.94, y = 0–0.075) phosphors were identified by a x-ray diffractometer (X'PERT PRO, Panalytical) with Cu $K\alpha$ (1.5406 Å) radiation in the range of $2\theta = 10-80^{\circ}$ operated at 40kV and 20 mA. The reflectance spectra were measured by a BaSO₄ powder calibrated UV visible spectrophotometer (Shimadzu, UV-2550) in the range of 250-750 nm. The photoluminescence emission (PL) and excitation (PLE) spectra of samples were recorded on the Hitachi F-4600 fluorescence spectrophotometer equipped with a 150W xenon lamp. The quantum efficiency of the as-synthesized phosphors was measured using a OY-2000 equipped with a 450W Xe lamp. The standard reference is Al₂O₃. The particle size and morphology of the phosphors were observed via a scanning electron microscopy (SEM) (NoVaTM Nano SEM 430). The electroluminescent emission spectra and the Commission Internationale de I'Eclairage (CIE) color coordinates of all LEDs were obtained by using a PMS-50 spectrophotocolorimeter (Everfine Co., LTD) with an integrating sphere under the 20 mA forwardbias current. All measurements were conducted at the room temperature.

3. Results and discussion

3.1. Crystal structures

Figure 1 presents the XRD patterns of $Y_{2.94-x}Lu_xAl_5O_{12}$: 0.06Ce³⁺ (x = 0-2.94) phosphors in the range of (A, $2\theta =$ 10–80°) and (B, $2\theta = 26-40^{\circ}$). All of the diffraction peaks are strong and similar, which are well indexed to the standard compound Al₅Y₃O₁₂ (JCPDS: 33-0040) and Lu₃Al₂Al₃O₁₂ (JCPDS: 18-0761) at x = 0 and 2.94, respectively. It can be shown that all samples are well-crystallized and single-phase of cubic garnet structure with the Ia-3d (230) space group. Any significant phase change and intermediate phase cannot be observed. As the radius of Lu³⁺ and Y³⁺ are similar, LuAG is the isostructural to YAG [21-23]. So the crystal structure remains constant when Lu^{3+} ions substitute for Y^{3+} ions in the whole area. In comparison with pure YAG, the diffraction peaks shift toward larger angles with increasing Lu concentration, due to the smaller ion radius of Lu^{3+} compared with Y^{3+} ions [20]. Hence, the smaller Lu^{3+} ions enter into the lattice, which are easy to replace Y^{3+} ions, occupying Y^{3+} sites and distorting the structure, resulting in the decrease of the lattice parameters. Finally, the host lattice has a trend of contraction which leads to the shift of the diffraction peaks toward larger 2θ value with increasing Lu³⁺ concentration (x = 0-2.94) as shown in figure 1(B). The uniform red-shift indicates that $Y_{2.94-x}Lu_xAl_5O_{12}:0.06Ce^{3+}$ compounds are formed as solid solutions in the whole range (x = 0-2.94).

3.2. Photoluminescence properties of $Y_{2.94-x}Lu_xAI_5O_{12}$:0.06Ce³⁺ (x = 0–2.94) phosphors

Figure 2(a) illustrates the diffuse reflectance spectra of typical $Y_{2.94}Al_5O_{12}$:0.06Ce³⁺ and Lu_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphors at room temperature. The reflectance bands of all the samples



Figure 1. XRD patterns of $Y_{2,94-x}Lu_xAl_5O_{12}$: 0.06Ce³⁺ (x = 0-2.94) phosphors in the range of (A, $2\theta = 10-80^\circ$) and (B, $2\theta = 26-40^\circ$).



Figure 2. (A) The diffuse reflection spectra of $Y_{2.94}Al_5O_{12}$: 0.06Ce³⁺ and Lu_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors; (B) the excitation and emission spectra of $Y_{2.94-x}Lu_xAl_5O_{12}$: 0.06Ce³⁺ (x = 0-2.94) phosphors. The inset is the normalized emission spectra. ($\lambda_{ex} = 450 \text{ nm}, \lambda_{em} = 507-532 \text{ nm}$).

are very similar. Both of the phosphors show three broad absorption bands covering the range from the UV to visible range. It can be observed that a platform of nearly 80% diffuse reflectance in the wavelength range of 530-750 nm, then it starts to decrease dramatically. The obvious absorption bands centered at 340 and 450 nm correspond to the allowed electric dipole transition of electrons from ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ ground state to the excited ${}^{2}D_{5/2}$, ${}^{2}D_{3/2}$ levels of Ce³⁺ ions, respectively [17, 23-25]. The origin of the band around $260\,\text{nm}$ may be a transition to the third 5d level and the absorption of host lattice [6]. From the reflectance spectra, it can be roughly calculated that the diffuse reflectance of Ce^{3+} ions around 340, 450 nm is about 50% and 56%, respectively. The absorption band at 450 nm can effectively absorb the blue emission from the commercially blue Ga(In)N chips in the range of 420-480 nm.

Furthermore, the slight blue-shift of Lu_{2.94}Al₅O₁₂:0.06Ce³⁺ in the reflectance spectra is observed for the Ce³⁺ absorption band around 450 nm. However, the absorption band around 340 nm show a red-shift compared with that of $Y_{2.94}Al_5O_{12}:0.06Ce^{3+}$ phosphor. The difference in the absorption bands reflects the strong influence of the local coordination on the 5*d* crystal field splitting. When Y³⁺ ions are completely replaced by smaller Lu³⁺ ions, a smaller crystal field splitting can be obtained between the two lowest 5 *d* levels of the five crystal field components in D₂ symmetry, which have been reported in the other literature [17, 26]. Thus, the increasing Lu³⁺ concentration shifts the lowest excited state energy level ²D_{3/2} to even higher energies, while shifting the second lowest excited state level ²D_{5/2} to lower energies.

The photoluminescence properties of $Y_{2.94-x}Lu_xAl_5O_{12}$: 0.06Ce³⁺ (x = 0-2.94) solid solutions are investigated and

Table 1. Internal quantum efficiency and parameters from the XRD data and emission spectra of the $Y_{2.94-x}Lu_xAl_5O_{12}:0.06Ce^{3+x}(x = 0-2.94)$ phosphors.

x	0	0.5	1.0	1.5	2.0	2.5	2.94
Intenal quantum efficiency (%)	66.03	73.63	76.38	78.46	87.39	91.76	92.49
Lattice (Å)	11.9939	11.9856	11.9690	11.9626	11.9366	11.9232	11.9038
FWHM (nm)	71	73	74	75	77	79	79
$\lambda_{\rm em} ({\rm nm})$	532	529	527	524	519	513	507
CIE x	0.3223	0.3114	0.3029	0.2913	0.2779	0.2610	0.2417
CIE y	0.6285	0.6294	0.6295	0.6284	0.6233	0.6170	0.6035



Figure 3. The CIE 1931 chromaticity diagram of $Y_{2.94-x}Lu_xAl_5O_{12}$: 0.06Ce³⁺ phosphors (∇ , x = 0-2.94) and the as-fabricated LEDs under $I_F = 20 \text{ mA}$ (\blacksquare).

shown in figure 2(b). The PL and PLE spectra of YLuAG:Ce are measured under 450nm excitation and different monitoring wavelengths varied from 507 nm to 532 nm. The effects of structure variations on the PL, PLE spectra and the luminescence efficiency can be observed obviously. From the PLE spectra (above), two high-efficiency broad bands are centered at 340 and 450 nm, which originate from ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ ground state to the excited ${}^{2}D_{5/2}$, ${}^{2}D_{3/2}$ level of Ce³⁺ ions [17, 23–25]. The intensity of excitation bands increases with varied Lu³⁺ concentration. The excitation band around 340 nm shows a red-shift, but the 450nm band shows a blue-shift with increasing Lu³⁺ concentration. All these results are consistent with the reflectance spectra as mentioned above. Furthermore, the strongest PLE peaks of all samples are around 450nm, which can be well matched the wavelength of blue Ga(In)N chips (420-480 nm).

The emission and normalized emission (to the peak intensity) spectra are displayed in figure 2(B) (below). YLuAG:Ce powders produce broad asymmetric emission bands ranging from 480 nm to 650 nm. The broad Ce³⁺ emission bands are assigned to the transition from the lowest 5*d* state ${}^{2}D_{3/2}$ to the ground state ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ transition accompanying with the vibronic coupling in the host lattice [9, 25]. The center of the emission bands shifts from 532 to 507 nm with increasing Lu^{3+} concentration. These emission shifts are ascribed to the tetragonal distortion around Ce^{3+} ions by chemical substitution in YLuAG host. As Lu^{3+} concentration increases, the crystal field splitting energy of the 5*d* state in Ce^{3+} ions decreases. So the lowest ${}^{2}D_{3/2}$ level shifts to higher energies and the emission of Ce^{3+} ions shows a blue-shift.

From figure 2(B), we can see that the emission intensity of the phosphors increases gradually with increasing Lu^{3+} content. Further investigation is examined and listed in table 1 by measuring the internal quantum efficiency of YLuAG phosphors. The internal quantum efficiency increase from 66.03% to 92.49% with Lu content varied from 0 to 2.94. Therefore, the increasing emission intensity of YLuAG phosphors is primarily due to the large absorption co-efficient of ionizing radiation with high quantum yield [27, 28]. And the result is different with the report that the Ce³⁺ emission intensity is slightly decrease with increasing Lu³⁺ concentration [20].

The parameters of phosphors are calculated from the emission spectra, as presented in table 1. Furthermore, the CIE chromaticity coordinates (x, y) of these phosphors shift from (0.3223, 0.6285) to (0.2417, 0.6035) with increasing Lu³⁺ concentration as shown in figure 3. Then the color of



Figure 4. Variation of the lattice parameters and the blue shift of Ce^{3+} emission as function of Lu^{3+} concentration in $Y_{2.94-x}Lu_xAl_5O_{12}$:0.06Ce³⁺ (x = 0–2.94) phosphors

 $Y_{2.94-x}Lu_xAl_5O_{12}:0.06Ce^{3+}$ (x = 0-2.94) phosphors can be tuned from the green–yellow to the green area with increasing Lu^{3+} concentration. Therefore, the LuAG phosphor can be used to create cool color temperature white LEDs with blue chips or applied in warm and high Ra white LEDs as the promising green component.

In addition, the correlation of the lattice parameters and the blue shift of Ce³⁺ emission as function of Lu³⁺ concentration in $Y_{2.94-x}Lu_xAl_5O_{12}$:0.06Ce³⁺ (x = 0-2.94) phosphors is demonstrated in figure 4. The lattice parameters are calculated to be 11.9939, 11.9856, 11.9690, 11.9626, 11.9366, 11.9232 and 11.9038 Å with varied x values, respectively, which are derived from the XRD data and listed in table 1. The substitution of Y³⁺ ions by smaller Lu³⁺ ions results in the lattice contraction and the lattice parameters decrease linearly with the increase of Lu³⁺ concentration. The result confirms that Y_{2.94-x}Lu_xAl₅O₁₂:0.06Ce³⁺ compounds are formed as solid solutions in the whole range (x = 0-2.94). It's worth noting that the emission peaks shift linearly with increasing Lu^{3+} content. Furthermore, the blue shift of the emission peak correlates very well with the lattice contraction. This result coincides with the previous reports about Gd³⁺ substitution for Y^{3+} in YAG host [9], and it can be concluded that the blue shift of the Ce³⁺ luminescence is predominantly originated from the lattice contraction.

3.3. Photoluminescence properties of $Lu_{3-y}AI_5O_{12}$:yCe³⁺ (y = 0–0.075) phosphors

In order to obtain the optimal doping concentration of Ce^{3+} ions, the PL and PLE spectra of $Lu_{3-y}Al_5O_{12}$: yCe^{3+} (y = 0-0.075) phosphors as the function of the activator concentration are measured under 450 nm excitation and 510 nm monitoring, as shown in figure 5. The features of Ce^{3+} emission on shape and peak position in the PL and PLE spectra have no obvious changes as the concentration increases. Both of them are ascribed to the allowed f-d transitions as disused above. The PL intensity enhances with the increase of Ce^{3+} content, and then reaches a maximum of y = 0.06. Subsequently, it decreases with further increase of Ce^{3+}



Figure 5. The excitation and emission spectra of $Lu_{3-y}Al_5O_{12}$: yCe³⁺ phosphors ($\lambda_{ex} = 450 \text{ nm}$, $\lambda_{em} = 510 \text{ nm}$).

concentration because of the concentration quenching process [5, 29, 30]. This reveals that the optimal doping concentration of Ce³⁺ ions in LuAG host is about 6%, which is in agreement with that of YAG:Ce phosphor reported by Tien *et al* [5]. It is noticed that the emission spectra shift slightly to the red region as the concentration of Ce³⁺ increase gradually. According to the previous reports, the red-shift tendency of emission peak is frequently observed in Ce³⁺-doped phosphors with increasing doping concentration, which is due to the lattice expansion from the substitution of Y³⁺ ions by larger Ce³⁺ ions [9].

3.4. SEM image of $Lu_{2.94}AI_5O_{12}$:0.06Ce³⁺ phosphor

The SEM images with different magnifications of Lu_{2.94} $Al_5O_{12}: 0.06Ce^{3+}$ powders are shown in figure 6. The uniform particles of Lu_{2.94}Al₅O₁₂:0.06Ce³⁺ with homogeneous microstructure are obtained by solid-state reactions with AlF₃ as a flux. The particles are dispersed evenly. Aggregation of these particles is not serious. The AlF₃ flux accelerates the crystallization and growth of grain size. It can be observed that most of the particles are the cubic garnet morphology with good crystallinity. The results are consistent with the XRD data depicted in figure 1. The average size of phosphors is estimated by approximately measuring 200 particles in Lu_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphor. Size is dependent on the diagonal length of particles. Therefore, the particle size distribution histogram can be obtained and confirms that the size of the sample show a good dispersion. Herein, the mean diameter of particles and geometric standard deviation of the phosphor powders are calculated to be 13.96 μ m and 3.02 μ m, respectively. For the application of the phosphors for white LED, the particle size and morphology should also be seriously considered, which influence the luminescence efficiency of phosphors and pc-LEDs. These results show that the synthesized phosphor is suitable for pc-LEDs packaging.



Figure 6. SEM images ((A) and (B)) and particles size distribution histogram (C) of Lu_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphor.



Figure 7. The electroluminescent spectra of the as-fabricated LEDs based on 450 nm blue Ga(In)N chips and $Y_{2.94-x}Lu_xAl_5O_{12}$:0.06Ce³⁺ (x = 0-2.94) phosphors under $I_F = 20$ mA.

3.5. The pc-LEDs with $Y_{2.94-x}Lu_xAI_5O_{12}$:0.06Ce³⁺ (x = 0–2.94) phosphors

Finally, pc-LEDs are fabricated with $Y_{2.94-x}Lu_xAl_5O_{12}$: 0.06Ce³⁺ (x = 0, x = 0.5, x = 1.0, x = 2.94) phosphors, silicones and blue Ga(In)N chips (~450 nm) in order to further investigation.

Table 2. Parameters of the as-fabricated LEDs based on 450 nm blue Ga(In)N chips and $Y_{2.94-x}Lu_xAl_5O_{12}$:0.06Ce³⁺ (x = 0-2.94) phosphors under $I_F = 20$ mA.

x	Luminous efficiency (lm W ⁻¹)	CIE <i>x</i>	CIE y	<i>Тс</i> (К)	Ra
0.0	68.52	0.2837	0.2808	10245	83.5
0.5	68.80	0.2784	0.2784	11230	83.0
1.0	73.20	0.2744	0.3038	11512	79.6
2.94	74.18	0.2466	0.3085	12635	67.8

The phosphor accounts for 20% of the mass of silicone and each phosphor is fabricated for five LED lamps. The electroluminescence spectra of the pc-LEDs under 20 mA forwardbias current (I_F) are presented in figure 7. The outlines of all electroluminescence spectra of LEDs are similar, which are coincide with those of reported pc-LEDs [31]. The spectra consist of two emission bands, one of the emission peaks around 450 nm belongs to blue chips, and the 520 nm peak is ascribed to the Ce³⁺ emission of YLuAG:Ce phosphors excited by 450 nm Ga(In)N chips. It is confirmed that the YLuAG:Ce materials can absorb the light of 450 nm efficiently, and convert it into green-yellow light. Furthermore, the relative intensity of YLuAG:0.06Ce³⁺ phosphors increases with the increasing Lu³⁺ concentration, which is in agreement with the result from the emission spectra shown in figure 2(B).

In addition, the average value of luminous efficiency, CIE chromaticity coordinates (x, y), color temperature Tc and color rendering index Ra of the pc-LEDs are calculated and listed in table 2. From the data, the luminous efficiency of pc-LEDs enhances gradually, reaches the maximum of 74.18 lm W⁻¹. The change of luminous efficiency of pc-LEDs is consistent with the result of the quantum efficiency, which confirms that the quantum efficiency of Ce³⁺ ions in YLuAG host increase with elevating Lu^{3+} content. The value of *Ra* decreases severely from 83.5 to 67.8, while the value of Tc increases. All of the Tcvalues of these packaging LEDs exceed 7000 K, revealing that they are cold light source. Furthermore, different pc-LEDS have various CIE chromaticity coordinates (x, y). As Lu³⁺ content increases, the corresponding CIE chromaticity coordinates of pc-LEDS shifted obviously in CIE 1931 chromaticity diagram, as presented in figure 3. It demonstrates that the different luminescent characteristics of the phosphors can regulate the properties of pc-LEDs. Therefore, the Lu³⁺ ion has a very important impact on the optical properties of YLuAG:Ce phosphors and the pc-LEDs. All these results confirm that LuAG:Ce phosphor exhibit higher emission efficiency than that of commercially YAG:Ce. And LuAG:Ce can be a promising green phosphor for white LEDs.

4. Conclusions

Lu³⁺ and Ce³⁺ doped YLuAG solid solutions have been successfully prepared. The well-crystallized cubic garnet phosphors exhibit high efficient excitation bands around blue areas, intensive and tunable emission spectra from yellow to green regions. A linear relationship between the lattice contraction and the blue shift of Ce3+ can be observed by substituting Lu³⁺ for Y³⁺. Furthermore, the quantum efficiency and emission intensity of phosphors enhances gradually with increasing Lu³⁺ content. The concentration quenching of Ce³⁺ ions in LuAG phosphors is about 0.06 mol. And the mean size of LuAG:Ce³⁺ phosphors are estimated to be 13.96 μ m. The fabricated LEDs based on 450nm Ga(In)N chips and YLuAG:Ce phosphors show the cool color white light. And the luminous efficiency of pc-LEDs can be improved 8% when Y³⁺ ions are completely substitute by Lu³⁺ ions. All results show that LuAG:Ce phosphor has excellent properties than these of commercially YAG:Ce and can be a good phosphor for cool color temperature white LEDs. Furthermore, it can also be the promising green component in warm white LEDs with high Ra.

Acknowledgments

This work is supported by Science and Technology Projects of Guangdong Province (2015A090905010), Innovative Research Team in University of Guangdong (2015KCXTD027), Technology Projects of Jiangmen (Jiang Cai Gong (2014) 173).

References

- [1] Nakamura S, Mukai T and Sench M 1994 Appl. Phys. Lett. 64 1687
- [2] Boukerika A and Guerbous L 2015 Opt. Mater. 40 14
- [3] Chen D, Xiang W, Liang X, Zhang J, Yue H, Din M G, Lu H and Ji Z 2015 J. Eur. Ceram. Soc. 35 859
- [4] Xie M B, Zhu G X, Pan R K, Li D Y and Hou D J 2016 J. Phys. D:Appl. Phys. 49 225105
- [5] Tien T Y, Gibbons E F, DeLosh R G, Zacmanidis P J, Smith D E and Stadler H L 1973 J. Electrochem. Soc. 120 278
- [6] Bachmann V, Ronda C and Meijerink A 2009 Chem. Mater. 21 2077
- [7] Ye S, Xiao F, Pan Y X, Ma Y Y and Zhang Q Y 2010 Mater. Sci. Eng. R 71 1
- [8] Abdullah M, Okuyama K, Lenggoro I W and Taya S 2005 J. Non-Cryst. Solids 351 697
- [9] Pan Y X, Wang W, Liu G K, Skanthakumar S, Rosenberg R A, Guo X Z and Li Kewen K 2009 J. Alloys Compd. 488 638
- [10] Seijo L and Barandiarán Z 2016 RSC Adv. 6 25741
- [11] Yang H and Kim Y 2008 J. Lumin. **128** 1570
- [12] Kolesnikov I E, Povolotskiy A V, Tolstikova D V, Manshina A A and Mikhailov M D 2015 J. Phys. D: Appl. Phys. 48 075401
- [13] Shi Y R, Wang Y H, Wen Y, Zhao Z Y, Liu B T and Yang Z G 2012 Opt. Express 20 21656
- [14] Setlur A A, Heward W J, Hannah M E and Happek U 2008 Chem. Mater. 20 6277
- [15] Sopicka-Lizer M, Michalik D, Plewa J, Juestel T, Winkler H and Pawlik T 2012 J. Eur. Ceram. Soc. 32 1383
- [16] Zorenko Y V 2000 Opt. Spectrosc. 88 551
- [17] Wu J L, Gundiah G and Cheetham A K 2007 Chem. Phys. Lett. 441 250
- [18] Li J G, Li J K, Zhu Q, Wang X J, Li X D, Sun X D and Sakka Y S 2015 RSC Adv. 5 59686
- [19] Zhang K, Liu Q F, Liu Q, Shi Y and Pan Y B 2010 J. Comb. Chem. 12 453
- [20] Shao Q Y, Dong Y, Jiang J Q, Liang C and He J H 2011 J. Lumin. 131 1013
- [21] Babin V, Gorbenko V, Krasnikov A, Makhov A, Nikl M, Zazubovich S and Zorenko Y 2010 Radiat. Meas. 45 331
- [22] Shannon R D 1976 Acta Crystallogr. A 32 751
- [23] Robbins D J 2007 J. Electrochem. Soc. 126 1550
- [24] Li H L, Liu X J and Huang L P 2007 Opt. Mater. 29 1138
- [25] Kim H T, Kim J H, Lee J K and Kang Y C 2012 Mater. Res. Bull. 47 1428
- [26] Ogiegło J M, Zych A, Ivanovskikh K V, Jüstel T and Ronda C R and Meijerink A 2012 J. Phys. Chem. A 116 8464
- [27] Koch A, Peyrin F, Heurtier P, Ferrand B, Chambaz B, Ludwig W and Couchaud M 1999 Proc. SPIE 3659 170
- [28] Zorenko Y, Gorbenko V, Konstankevych I, Voloshinovskii A, Stryganyuk G, Mikhailin V, Volobanov V and Spassky D 2005 J. Lumin. 114 85
- [29] Holloway W W and Kestiglan M 1969 J. Opt .Soc. Am. 59 60
- [30] Zhou W, Ma X X, Zhang M L, Luo Y and Xia Z G 2015 Ceram. Int. 190 43
- [31] Bois C, Bodrogi P, Khanh T Q and Winkler H 2014 J. Solid State Light. 1 5