Journal of Alloys and Compounds 523 (2012) 151–154

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Brownish red emitting YAG:Ce^{3+},Cu^{+} phosphors for enhancing the color rendering index of white LEDs

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ARTICLE INFO

Article history:
Received 22 November 2011
Received in revised form 18 January 2012
Accepted 24 January 2012
Available online 9 February 2012

Keywords:
Cu^{+}
Co-precipitation
Electroluminescence spectra
YAG
Phosphors

ABSTRACT

The optical properties of Cu^{+} and Ce^{3+} co-doped $Y_3Al_5O_{12}$ synthesized by co-precipitation method are investigated in detail. Doping Cu^{+} ion into the YAG has little effect on the crystallized structure but the energy levels of Ce^{3+} ions have been changed. After doping with Cu^{+}, the intensity of the broad emission band in the range of 580–700 nm has been enhanced under the visible region excitation light (400–500 nm) compared with that of undoped sample. Two broad emission bands of the electroluminescence spectra centered at around 540 nm (yellow) and 630 nm (red) are observed via a downconversion process under blue light (λ_{em} = 460 nm) excitation. Meanwhile, the red region of the electroluminescence spectra has been enlarged. Hence, Cu^{+} doping could be an effective method to enhance the red light proportion in white LEDs.

1. Introduction

The past 10 years have seen rapid development in GaN-based light emitting diode (LED) technology, especially focused on advanced solid state white lighting sources. To achieve white light from LEDs, strategies involve in assembling several LED chips of different color lights, using quantum dots to down-convert higher energy light or using phosphors to down-convert near-UV and blue light [1–4]. Among the three strategies, the third is the most popularly used method in the LED industry due to its advantages such as high efficiency, long lifetime, physical stability, a mercury-free design and color stability.

Currently, the LED phosphor market is dominated by the YAG phosphor. The characteristic emission spectrum of blue LED chip is in the range of 400–480 nm. The YAG phosphors absorb blue light partially and emit yellow-green light in the range of 500–700 nm. The combination of the blue light emitted by GaN chip and yellow-green light emitted by YAG produces white light [5]. Because the particular property of the YAG crystal field, this material suffers a low red region emission when it is excitated by a blue LED chip. For this reason, the white LEDs have lower color rendering index [5]. Many researchers had made great efforts to develop new LED phosphors including silicates, aluminates, sulfides, phosphates, borates, nitrogen-oxides, oxides, nitrides, molybdates host [6–17]. But these materials have some shortcoming more or less, such as bad physical and chemical stability. Therefore, YAG phosphor has obvious superiority in the next years although it needs to be optimized.

At present, doping trace elements into the host is the principal approach for enhancing the red proportion of emission spectra of the YAG phosphors. Moriga and Pan et al. reported the emission wavelength shifted to the longer wavelength due to the crystal lattice expansion associated with an increase of gadolinium content, but the intensity decreased sharply [18,19]. Jang, Yang, Lin, and Wang et al. doped Pr, Tb, Mn and Sm into the YAG [20–24]. Yang et al. and Lee et al. doped the Eu into garnets [25,26]. Setlur et al. doped the incorporation of Si^{4+}–N^{3-}, Mg, Si into the YAG [27,28]. Chen et al. doped the Sr into the YAG [29,30]. The results demonstrated that these methods could not provide enough impact on enhancing red region. Furthermore, these ions led to many negative effects, such as decrease of intensity.

In this paper, Cu^{+} ion was doped into the YAG to enhance the red proportion, and the microstructure and luminescence properties of synthesized materials were studied via XRD, PL. It was found that the emission in the range of 600–700 nm was improved after doping this element, and the red region of the electroluminescence spectra of the doped YAG:Ce^{3+} phosphors is broader than that of un-doped sample. Hence, doping Cu^{+} ion into the YAG has great potential to enhance the color rendering index of the white LED.

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doi:10.1016/j.jallcom.2012.01.131

2. Experimental

2.1. Preparation

Copper-doped YAG:Ce^{3+} phosphors $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:0.06$Ce^{3+}$ (x = 0–0.1) were synthesized via co-precipitation method. In this method, the nitrates of yttrium, aluminum, copper and cerium were mixed together in the distilled water. The ammonium bicarbonate dissolved in the distilled water was used as precipitator. The metal ions/ammonium bicarbonate molar ratio was 1:4. The ammonium bicarbonate solution was added into the well-mixed nitrate solution via positive titration. The precursor obtained was calcined at 850 °C under the atmosphere with a heating rate of 5 °C/min to emancipate the carbon dioxide and vapour. 3 wt.% BaF_2 was added into the rough powders as the flux. After a good mixing in an agate mortar, the mixture was sintered at 1300–1500 °C for 3 h under the reducing atmosphere (N_2/H_2 = 95:5) in order to obtain the YAG:Ce^{3+} phosphors [31]. The phosphors obtained were incorporated respectively into a device. Relevant parameter were based on a mature technology, and the detailed parameters were listed as follows: roasted temperature is 150 °C, roasted time is 1.5 h, the ratio of silica gel A/silica gel B/phosphors = 40:40:1.

2.2. Characterizations

XRD characterization was performed on a X-ray powder diffractometer (SHIMADZU XRD-6000) with Cu K_α radiation (λ = 0.15405 nm). Photoluminescence (PL) excitation and emission spectra of phosphors were recorded on a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp (scanning rate = 1200 nm/s, slit width = 5 nm, and PMT voltage = 400 V) as the excitation source. The electroluminescence spectra of the device (blue chip + phosphors) were obtained from a photoelectric color integrated test system (HSP-6000, HongPu, China). All the measurements were performed at room temperature.

3. Results and discussion

3.1. Crystal structure

The crystallographic phase of $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:0.06$Ce^{3+}$ (x = 0–0.1) were studied by X-ray diffraction (XRD). The YAG belongs to the cubic structure with a = 1.2009 nm and Ia3d lattice symmetry. It is well known that only pure YAG is favorable for luminescence [33], while the intermediate phases such as $YAlO_3$ (YAP, polymorph) and $Y_4Al_2O_9$ (YAM, monoclinic) do not favor luminescence. Generally, these intermediate phases appear after the Y_2O_3–Al_2O_3 was sintered below 1300 °C [34]. The result shown in Fig. 1 indicates that the YAG phase matches well with the JCPDS card No. 33-0040 even after Cu^+ ion doping (x = 0, 0.1). It indicates that the doping of a little amount of Cu^+ ion has little effect on the YAG crystallized structure.

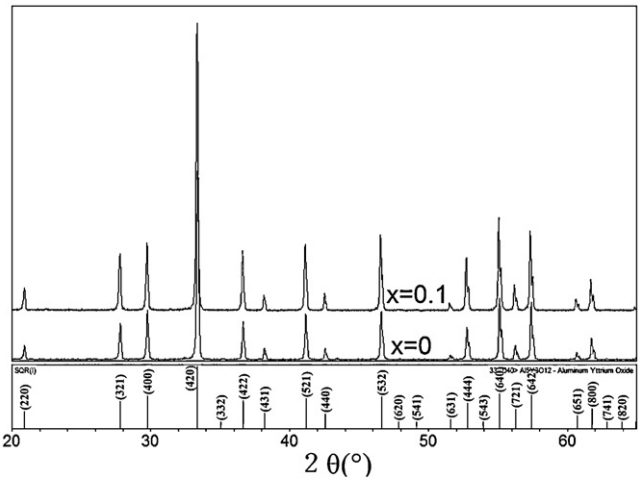

Fig. 1. XRD patterns of the $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:0.06$Ce^{3+}$ with x = 0, 0.1 phosphors.

3.2. Photoluminescence properties

Ce^{3+} has only one electron in the 4f state. This state is split into $^2F_{7/2}$ and $^2F_{5/2}$, their D-value of the energy is about 2200 cm^{-1}. The next upper state is 5d state, and the two states transitions are parity and spin allowed. Affected by the crystal field of YAG, the 5d state is split into five states [32–37]. Hence, there are two trivalent Ce^{3+} ion absorption bands which locate at 342 nm and 451 nm (as shown in Fig. 2a) in the excitation spectra. The intensity of excitation band within 390–520 nm is the higher one and provides a strong basis to make use of the as-prepared YAG phosphors with GaN chip to generate white light. The emission of the commercially available GaN chip is in the range of 400–480 nm. Hence, YAG phosphors + GaN chip is an ideal group to prepare white LED.

Fig. 2 shows the effects of doping Cu^+ ion on the photoluminescence properties of YAG:Ce^{3+} phosphors. Typical emission spectra of YAG:Ce^{3+} phosphors show an intense green-yellow emission in the range of 500–700 nm under the 460 nm excitation (as shown in Fig. 2a). It is interesting to note that the integral emission intensity decreases with the addition of the Cu^+ ion, while the intensity of the broad emission band in the range of 580–700 nm has been enhanced (as shown in Fig. 2b). Comparing with the excitation spectra of the YAG:Ce^{3+} phosphors without doping Cu^+ ion, it is found that Cu^+ (x = 0.1) doping makes an excitation wavelength peak shift from 342 nm to 340 nm, while the other peak shift from 451 nm to 457 nm. The distance of the two peaks was expressed by

$$\Delta\lambda_{ex21} = \lambda_{ex2} - \lambda_{ex1} \quad (1)$$

where λ_{ex1} stands for the excitation peak of $^2F_{5/2} \rightarrow {}^2D_{5/2}$, and λ_{ex2} stands for the excitation peak of $^2F_{5/2} \rightarrow {}^2D_{3/2}$.

Table 1 summarizes the excitation wavelength, the emission wavelength and the distance between the two peaks. The distance ($\Delta\lambda_{ex21}$) increased 8 nm dramatically after the doping of Cu^+ ion. The phenomenon indicates that Cu^+ ion make the $^2D_{5/2}$ level rise and the $^2D_{3/2}$ level descend (as shown in Fig. 3a). Descent of the

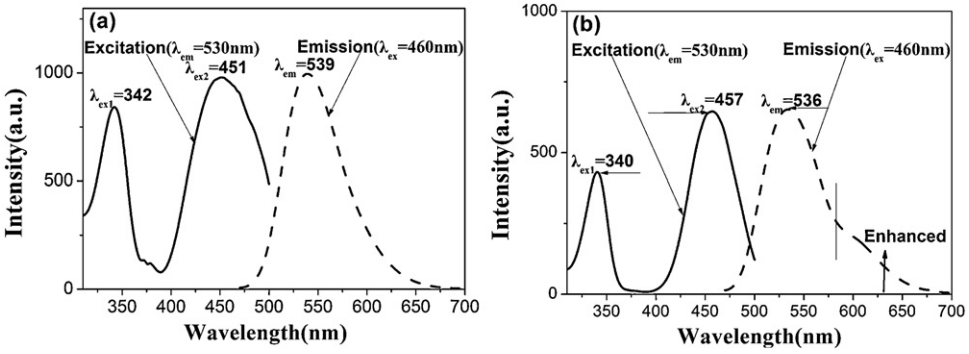

Fig. 2. Comparison of excitation and emission spectra of $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:0.06$Ce^{3+}$ phosphors (x = 0 and x = 0.1), (a) excitation and emission spectra of $Y_{2.88}Al_5O_{12}$:0.06Ce^{3+} phosphors and (b) excitation and emission spectra of $Y_{2.88}Al_{4.9}Cu_{0.1}O_{12}$:0.06$Ce^{3+}$ phosphors.

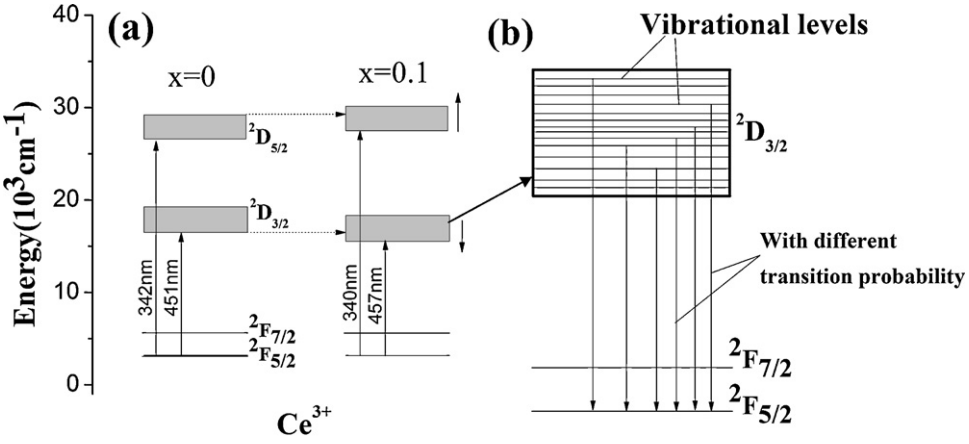

Fig. 3. (a) Transformation of 5d orbital energy level of Ce^{3+} ion in the YAG:Ce^{3+} phosphors with Cu^+ ion doping ($x = 0.1$) and (b) $^2D_{3/2}$ level diagrams.

Table 1
Comparison of excitation and emission wavelength and $\Delta\lambda$ for different Cu^+ ion concentration in YAG:Ce^{3+} phosphors.

Sample	λ_{ex1} (nm)	λ_{ex2} (nm)	$\Delta\lambda_{ex21}$ (nm)	λ_{em} (nm)
$x = 0$	342	451	9	539
$x = 0.1$	340	457	17	536

$^2D_{3/2}$ level minished the gap energy of the $^2D_{3/2}$-4f. However, the emission wavelength shifts 3 nm to blue color with the addition of the Cu^+ ion. It is well known that the fracturing level contains many vibrational levels. The electrons on the vibrational levels have different transition probability (as shown in Fig. 3b). Cu^+ ion doping makes transition probable density redistribute. Furthermore, it changes the form of the emission spectra and enhances the red proportion.

3.3. Electroluminescent properties

The samples $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:$0.06Ce^{3+}$ ($x = 0$, 0.1) were incorporated respectively into a device to compare their electroluminescence properties. Fig. 4a shows the electroluminescence spectra of two white LEDs. The region of the phosphor emission spectra is in the range of 500–700 nm. It is interesting to note that doping Cu^+ ion makes the single peak develop into two peaks (as shown in Fig. 4b). Furthermore, the red region of the emission spectra of the $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:$0.06Ce^{3+}$ ($x = 0.1$) is broader than that

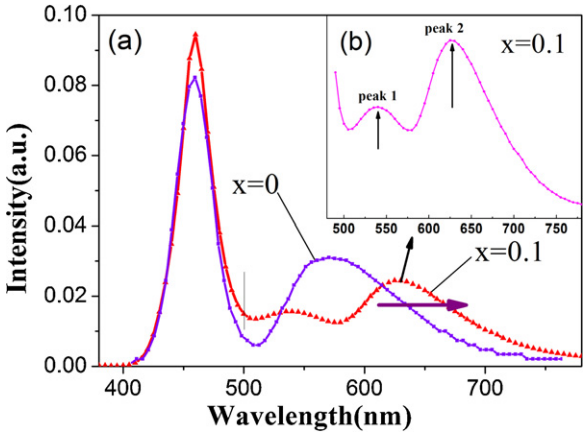

Fig. 4. (a) Emission spectrum of the two white LEDs with $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:$0.06Ce^{3+}$ ($x = 0$, 0.1) phosphors and (b) the partial emission spectra of the white LED with $x = 0.1$ phosphor.

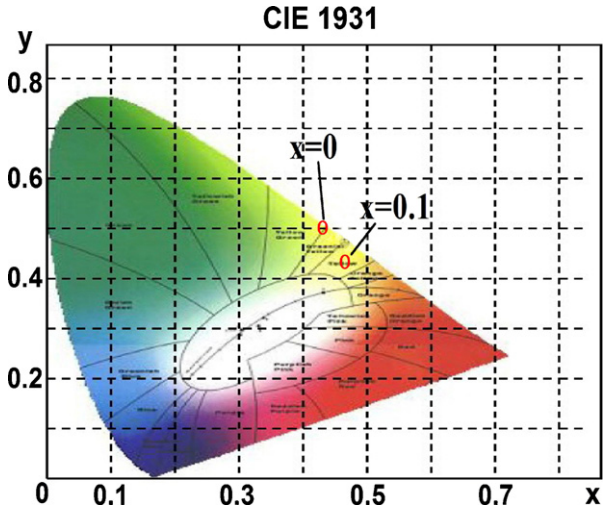

Fig. 5. CIE 1931 chromaticity of $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:$0.06Ce^{3+}$ ($x = 0$, 0.1) phosphors under excitation by blue LED chip.

of $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:$0.06Ce^{3+}$ ($x = 0$). It is well known that the color rendering index of illuminant depends on the spectra of the emission light. Many researchers pointed out that the more numbers of the simplex lights have, the higher color rendering index of the light was (as shown in Fig. 6) [38]. In the present, after doping

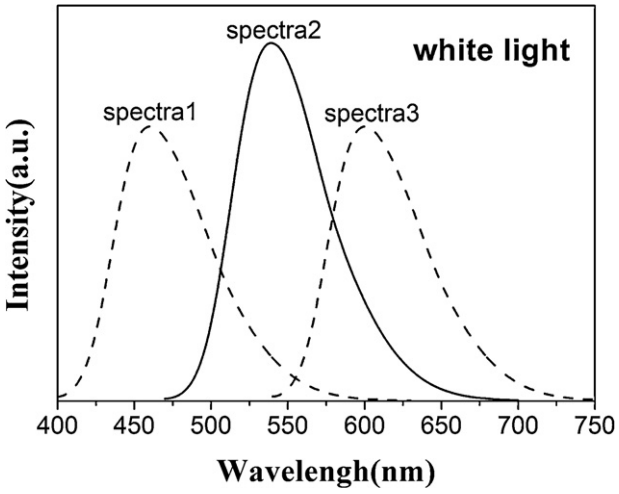

Fig. 6. Schematic diagram of the spectra of the white light.

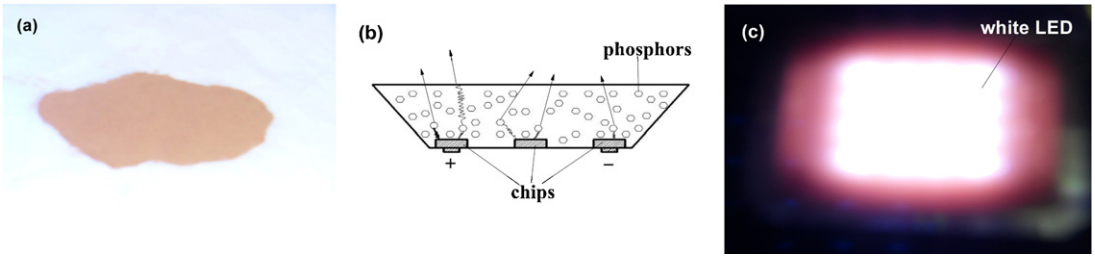

Fig. 7. (a) Photograph of the $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:0.06$Ce^{3+}$ of $x = 0.1$, (b) scheme of new white LED, and (c) image of a LED under a 12 V voltage and 80 mA forward bias.

Table 2
Comparison of colorimetric coordinates (x_c, y_c) with the different Cu^+ ion concentration in YAG:Ce^{3+} phosphors.

Sample	Red (%)	Green (%)	Blue (%)	x_c	y_c
$x = 0$	13.3	85.8	0.9	0.4098	0.5459
$x = 0.1$	22.7	76.9	0.4	0.4653	0.4864

adequate Cu^+ ion, the area of the emission spectra was changed and the color rendering index of the white LED was improved.

The colorimetric coordinates (x_c, y_c) for the YAG phosphors were calculated by equidistant wavelength method [39]. The colorimetric coordinates of the two samples are shown in Fig. 5. Generally, when red-shift happens in the emission wavelength, the colorimetric coordinate (x_c, y_c) is closer to red region. After Cu^+ ion was doped blue shift happened, but the colorimetric coordinates (x_c, y_c) of the sample ($x = 0.1$) is closer to red region than the sample without doping Cu^+ ion ($x = 0$). It indicates that the ratio of red has been increased. The colors ratio of the spectra and the colorimetric coordinates (x_c, y_c) of the phosphors as-prepared are summarized and shown in Table 2. The measured values of ratio of red and green in sample ($x = 0$) were 13.3% and 85.8% respectively. After doping Cu^+ ion into the YAG, the red ratio has increased to 22.7%, while the green ratio has decreased to 76.9%.

Normally, the color of the YAG:Ce^{3+} phosphors is green-yellow. However, the powders' color was changed into brownish after doping Cu^+ ion ($x = 0.1$) into the YAG (as shown in Fig. 7a). Fig. 7b shows the schematic diagram of the white LED as integrated. It shows obviously that the light composition of the LED adopting $Y_{2.88}Al_{(5-x)}Cu_xO_{12}$:0.06$Ce^{3+}$ ($x = 0.1$) phosphors has more red proportion (as shown in Fig. 7c). Therefore, Cu^+ ion doping is an effective method to enhance the color rendering index of the white LEDs.

4. Conclusion

In conclusion, we have obtained enhanced red region PL emission by doping Cu^+ ion. Cu^+ ion doping has little effect on the crystalline structure. The electroluminescence spectra of the YAG phosphors have been changed and developed into two peaks. Doping Cu^+ ion into the YAG makes the ratio of red increase. Furthermore, the as-prepared phosphors could be encapsulated with blue chips to produce white light. This YAG:Ce^{3+},Cu^+ phosphors have higher color rendering index.

Acknowledgment

The authors would like to acknowledge project supported by the Program for New Material Development & Application Innovative Research Team of Higher Education in ChongQing of China (Grant No. 201042).

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