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# $Ce^{3+}$ doped $BaLu_2Al_4SiO_{12}$: A promising green-emitting phosphor for white LEDs

Yaochun Qiang[a,b], Zhifang Pan[b,c], Xinyu Ye[b,c,*], Mingzhang Liang[a,b], Jianfei Xu[a,b], Jianhui Huang[a,b], Weixiong You[a,b,*], Huali Yuan[d]

[a] College of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, PR China
[b] Jiangxi Key Laboratory of Rare Earth Luminescence Materials and Devices, Jiangxi University of Science and Technology, Ganzhou 341000, PR China
[c] College of Metallurgy and Chemistry Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, PR China
[d] College of Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, PR China

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ABSTRACT

$BaLu_{1.94}Al_4SiO_{12}$:0.06$Ce^{3+}$ (BLASO:0.06$Ce^{3+}$) green-emitting phosphor could be easily obtained by a conventional solid-state reaction method at 1400 °C. BLASO:0.06$Ce^{3+}$ possesses the garnet structure (*Ia*$\bar{3}$*d* space group) with the lattice parameter a = 11.9222(0) Å. The emission peak of BLASO:0.06$Ce^{3+}$ is located at 513 nm and its photoluminescent quantum yield is determined to be 92.4% at 25 °C when excited at 450 nm. BLASO:0.06$Ce^{3+}$ presents excellent thermal properties, with the photoluminescence intensity at 200 °C only decreased to 91.5% of its room temperature value. A phosphor-converted white LED device fabricated by using BLASO:0.06$Ce^{3+}$ as the green phosphor exhibits good optical performance with Ra = 88.5, CCT = 3562 K and CIE1931 chromaticity coordinates as (x = 0.4041, y = 0.3951). The results indicate that BLASO:0.06$Ce^{3+}$ phosphor has strong potential applications in developing high color rendering, thermally stable, warm-white LEDs.

## 1. Introduction

In the past two decades, white light-emitting diodes (LEDs) have been well developed and widely applied to replace traditional lighting devices due to their excellent properties such as higher efficiency, longer lifetime, better reliability, and so on [1–3]. Generally, white LEDs are fabricated by combining blue LEDs and yellow phosphors, whose luminous efficiency is very high but with low Ra value and high correlated color temperature (CCT) [4–8]. In order to improve the Ra value of white LEDs, a different type of white LEDs was created by combining blue LED chips and green phosphors and red phosphors [9–12]. The Ra value of this type of white LEDs is even more than 90. Therefore, it can be concluded that green phosphors play a key role in fabricating high Ra white LEDs.

$Lu_3Al_5O_{12}:Ce^{3+}$ phosphor is almost an ideal green-emitting phosphor for white LEDs, which exhibits high photoluminescent quantum yield (QY) [13] and excellent luminescence thermal stability [13,14], but its main raw material, $Lu_2O_3$, is one kind of rare earth oxides, which makes $Lu_3Al_5O_{12}:Ce^{3+}$ very expensive. Hence, we are interested in decreasing the usage of $Lu_2O_3$ in $Lu_3Al_5O_{12}:Ce^{3+}$.

It has been reported that a double substitution of $Ca^{2+}$-$Si^{4+}$ for $Lu^{3+}$-$Al^{3+}$ in $Lu_3Al_5O_{12}:Ce^{3+}$ could reduce the usage of $Lu_2O_3$, but the photoluminescent intensity and thermal stability of the developed $CaLu_2Al_4SiO_{12}:Ce^{3+}$ phosphor were much worse than those of $Lu_3Al_5O_{12}:Ce^{3+}$ phosphor [15]. Ji et al. [16] reported that a double substitution of $Ba^{2+}$-$Si^{4+}$ for $Y^{3+}$-$Al^{3+}$ in $Y_3Al_5O_{12}:Ce^{3+}$ could decrease the usage of $Y_2O_3$ and the obtained $BaY_2Al_4SiO_{12}:Ce^{3+}$ phosphor still maintains excellent performance. Therefore, we intend to employ 1 mol $Ba^{2+}$-$Si^{4+}$ ion pairs to replace1 mol $Lu^{3+}$-$Al^{3+}$ ion pairs in $Lu_3Al_5O_{12}:Ce^{3+}$ phosphor in order to cut down the usage of $Lu_2O_3$ and maintain its good performance.

In this study, $Ce^{3+}$ doped $BaLu_2Al_4SiO_{12}$ green-emitting phosphors were prepared by a solid-state reaction method. The crystal structure of $BaLu_{1.94}Al_4SiO_{12}$:0.06$Ce^{3+}$ was analyzed, and then the photoluminescent QY, thermal quenching of luminescence and thermal color shift of $BaLu_{1.94}Al_4SiO_{12}$:0.06$Ce^{3+}$ were investigated and compared with those of two commercially available green-emitting phosphors, $(Sr,Ba)_2SiO_4:Eu^{2+}$ (YH-S525M, Hangzhou YingHe photoelectric materials Co., Ltd.) and $Lu_3Al_5O_{12}:Ce^{3+}$ (GAP535-L, Raypower Optoelectronics (Suzhou) Co., Ltd.). Meanwhile, the optical properties of the white LED made by combining a blue LED (emission peak at 465 nm) with the prepared $BaLu_{1.94}Al_4SiO_{12}$:0.06$Ce^{3+}$ and a commercial red nitride phosphor ($(Ca,Sr)AlSiN_3:Eu^{2+}$ 640 nm) were measured.

* Corresponding authors at: College of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, PR China.
*E-mail addresses:* xinyye@gmail.com (X. Ye), you_wx@126.com (W. You).

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## 2. Experimental

### 2.1. Synthesis of BLASO:$Ce^{3+}$ phosphor

The samples of $BaLu_{2-x}Al_4SiO_{12}$:$xCe^{3+}$ (BLASO:$xCe^{3+}$, $x$ = 0, 0.01, 0.02, 0.03…0.08) were prepared by using a conventional solid-state reaction method. Starting materials consisting of stoichiometric amounts of $BaCO_3$ (99.8%), $Lu_2O_3$ (99.99%), $Al_2O_3$ (99.99%), $SiO_2$ (99.99%) and $CeO_2$ (99.99%) were fully grounded with an agate mortar and pestle. After mixing for 1 h, the mixture was placed in alumina crucibles, and then fired at 1400 °C for 4 h in a weakly reducing atmosphere (5 v% $H_2$ / 95 v% $N_2$). After the cooling, the obtained samples were crushed, and grounded with an agate mortar and pestle for 5 min.

### 2.2. Fabrication of phosphor-converted white LED

The prepared BLASO:0.06$Ce^{3+}$ (1.2 g) and the commercial red nitride phosphor ((Ca,Sr)$AlSiN_3$:$Eu^{2+}$ 640 nm, 0.02 g) were dispersed homogeneously into the silicone (4.0 g). The mixture was coated on a blue LED (465 nm), then the LED was baked in the oven for 40 min at 60 °C and then for 60 min at 120 °C.

### 2.3. Characterization

The crystal structure of the samples was analyzed by X-ray diffraction (XRD, X'Pert Powder, Nederland) using Cu Kα radiation. The diffuse reflection spectra (Scan slit 2 nm, Step 0.5 nm) of the samples were measured by a UV–VIS–NIR spectrometer (Lambda 950, PerkinElmer, America). The excitation and emission spectra at 296 K (Step 0.5 nm, Dwell time 0.3 s, Scan slit 0.2970 nm), emission spectrum at 12 K (Step 0.2 nm, Dwell time 0.3 s, Scan slit 0.8505 nm) and quantum yield (Step 0.5 nm, Dwell time 0.3 s, Scan slit 0.4387 nm) of the samples were measured by a fluorescence spectrometer (FLS980, Edinburgh Instruments, UK) with Xe-lamp (450 W) as an excitation source. The emission spectra, relative luminescence intensity and the CIE 1931 chromaticity coordinates of the samples at different temperatures (25–200 °C) were recorded by an exciting spectra and thermal quenching analyzer (EX-1000, Everfine, China). The optical properties of the white LED were measured by a high accuracy array spectroradiometer (HASS-2000, Everfine, China).

## 3. Results and discussion

### 3.1. Crystal structure of $Ce^{3+}$ doped BLASO

The XRD patterns of BLASO:$xCe^{3+}$ (x = 0.01, 0.02, 0.03… 0.08) samples are shown in Fig. 1. As can be seen, the diffraction peaks of the samples are matched well with that of the pure phase lutetium aluminium garnet ($Lu_3Al_5O_{12}$ JCPDS 18–0761) and no significant impurities or secondary phases are observed, which confirms that the obtained samples are single garnet phase. Fig. 2 shows the experimental diffraction pattern, calculated diffraction pattern and the difference profile of Rietveld refinement for BLASO:0.06$Ce^{3+}$. Rietveld refinement was conducted using $Lu_3Al_5O_{12}$ (ICSD 23846) as the model. As shown in Fig. 2, all the observed diffraction peaks are matched well with the calculated diffraction peaks. The refined crystallographic data of BLASO:0.06$Ce^{3+}$ are listed in Table 1. The low residual factors (Rwp = 5.25% and Rp = 3.95%) indicate that the validity of the refinement is high. As shown in Table 1, the crystal structure of BLASO:0.06$Ce^{3+}$ belongs to cubic crystal system with a space group of $Ia\bar{3}d$. The refined cell parameters are a = 11.9222(0) Å and V = 1694.61(1) $Å^3$. The crystallographic site coordinates, site occupancy factors, and equivalent isotropic displacement parameters are listed in Table 2. The results show that Ba is located on the 24c site (on the dodecahedra site), Si is located not only on the 16a site (on the

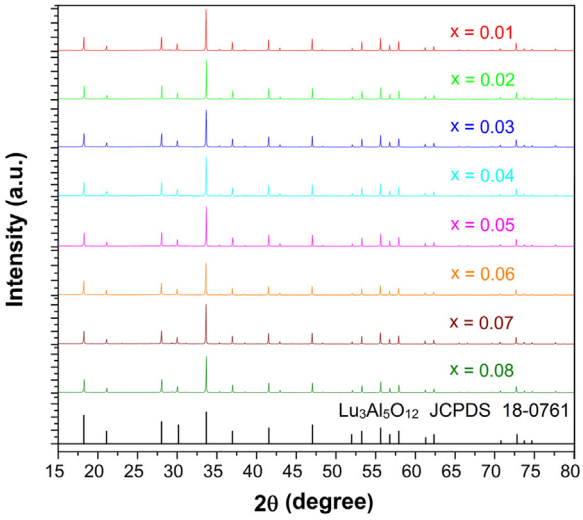


**Fig. 1.** XRD patterns of $BaLu_{2-x}Al_4SiO_{12}$:$xCe^{3+}$ ($x$ = 0.01, 0.02, 0.03… 0.08).

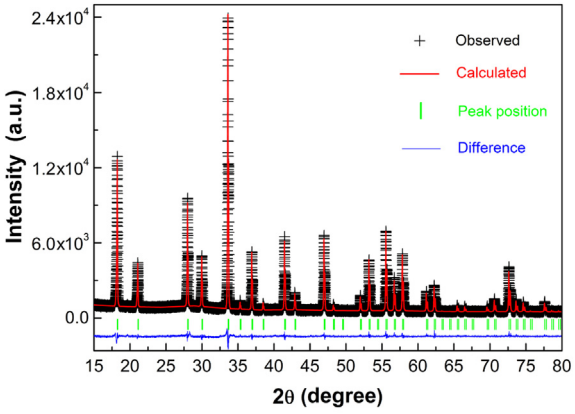


**Fig. 2.** Rietveld refinement XRD patterns of BLASO:006$Ce^{3+}$.

**Table 1**
Refined structural data of BLASO:0.06$Ce^{3+}$.

| Formula | $BaLu_{1.94}Ce_{0.06}Al_4SiO_{12}$ |
|---|---|
| **Crystal system** | Cubic |
| **Space-group** | $Ia\bar{3}d$ (230) |
| **Cell parameters** | a = 11.9222(0) Å |
| **Cell volume** | 1694.61(1) $Å^3$ |
| **Z** | 8 |
| **Calculated density** | 6.37472 $g/cm^3$ |
| **$R_{wp}$** | 0.0525 |
| **$R_p$** | 0.0395 |

**Table 2**
Fractional atomic coordinates and isotropic displacement parameters of BLASO:0.06$Ce^{3+}$.

| Atom | Wyck. | x/a | y/b | z/c | S.O.F. | $U_{iso}$ [$Å^2$] |
|---|---|---|---|---|---|---|
| Al1 | 16a | 0 | 0 | 0 | 0.68824 | 0.0071 |
| Al2 | 24d | 3/8 | 0 | 1/4 | 0.85173 | 0.0082 |
| Lu1 | 24c | 1/8 | 0 | 1/4 | 0.647 | 0.0056 |
| O1 | 96 h | − 0.03140 | 0.05275 | 0.15009 | 1 | 0.0099 |
| Ba1 | 24c | 1/8 | 0 | 1/4 | 0.333 | 0.0032 |
| Ce1 | 24c | 1/8 | 0 | 1/4 | 0.02 | 0.0055 |
| Si1 | 16a | 0 | 0 | 0 | 0.31176 | 0.0095 |
| SI2 | 24d | 3/8 | 0 | 1/4 | 0.14827 | 0.0106 |