



Article

# The Enhanced Red Emission and Improved Thermal Stability of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ Phosphors by Using Nano- $\text{EuB}_6$ as Raw Material

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**Abstract:** Synthesizing phosphors with high performance is still a necessary work for phosphor-converted white light-emitting diodes (W-LEDs). In this paper, three series of  $\text{CaAlSiN}_3:\text{Eu}^{2+}$  (denoted as  $\text{CASN}:\text{Eu}^{2+}$ ) phosphors using  $\text{Eu}_2\text{O}_3$ ,  $\text{EuN}$  and  $\text{EuB}_6$  as raw materials respectively are fabricated by under the alloy precursor normal pressure nitridation synthesis condition. We demonstrate that  $\text{CASN}:\text{Eu}^{2+}$  using nano- $\text{EuB}_6$  as raw material shows higher emission intensity than others, which is ascribed to the increment of  $\text{Eu}^{2+}$  ionic content entering into the crystal lattice. An improved thermal stability can also be obtained by using nano- $\text{EuB}_6$  due to the structurally stable status, which is assigned to the partial substitution of  $\text{Eu-O}$  ( $\text{Eu-N}$ ) bonds by more covalent  $\text{Eu-B}$  ones that leads to a higher structural rigidity. In addition, the W-LEDs lamp was fabricated to explore its possible application in W-LEDs based on blue LEDs. Our results indicate that using  $\text{EuB}_6$  as raw materials can provide an effective way of enhancing the red emission and improving the thermal stability of the  $\text{CASN}:\text{Eu}^{2+}$  red phosphor.

**Keywords:** alloy precursors; nitride;  $\text{CaAlSiN}_3:\text{Eu}^{2+}$  red phosphor; nano- $\text{EuB}_6$

## 1. Introduction

White light-emitting diodes (W-LEDs) are considered as the next-generation solid-state lighting system due to the high luminous efficiency, long operation time, reliability environmental friendliness [1–3]. The traditional way used to obtain white light is combing blue InGaN LEDs chip with the yellow phosphor  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  ( $\text{YAG}:\text{Ce}^{3+}$ ). However, using a single yellow phosphor leads to low color rendering index ( $R_a < 80$ ) due to the insufficient red component in the spectra, making them unsuitable for high-quality “warmer” white lighting [4–7]. Therefore, a red emitting phosphor is thus essentially needed to enhance the red spectral part to achieve much higher color rendering indices.

Currently, several red emitting phosphors attract much attention and are pervasively studied due to the property of effectively enhancing the color rendition, such as  $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$  ( $\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$ ) [8–11],  $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$  [12–15] and  $\text{CASN}:\text{Eu}^{2+}$  [16–19]. Among the above red phosphors, the emission of  $\text{Eu}^{2+}$  in  $\text{CaAlSiN}_3$  host locates in deep red region and possesses the advantages of good thermal stability, reliability and high quantum efficiency, which make it superior to others.

There are many preparation methods in fabricating  $\text{CaSiN:Eu}^{2+}$  red phosphors each has its own shortcomings. Commonly, the metal and rare earth nitrides are used as raw materials in preparing  $\text{CaSiN:Eu}^{2+}$  red phosphors they have to be operated in glove box because nitride compounds are unstable, decomposable and oxidizable in the air hence, the ideas of inhibiting certain disintegrating process put higher requirements to the experimental equipment and additional standards of higher temperature ( $\geq 1800^\circ$ ) and pressure ( $\geq 1$  MPa) [20,21]. For example, experimental expensive and yield small amounts of outcome when it comes to spark plasma sintering (SPS) process [22,23] and self-propagating high temperature synthesis (SHS) procedures [19,24], therefore, it is difficult to be carried out in manufacturing. In contrast, the alloy precursor normal pressure nitridation process is easier to operate rested upon high active alloy without high temperature ( $\geq 1800^\circ$ ) and high pressure ( $\geq 1$  MPa) requirement, whereas the oxidation of the raw material is difficult to avoid. Higher oxygen content in raw materials necessitates it to be processed with oxidation-reduction treatment. To this end, several very simple methods like gas reduction nitridation (GRN) method [25,26] and carbothermal reduction and nitridation (CTRN) method [27,28] are applied to the preparation of  $\text{CaSiN:Eu}^{2+}$  nitride materials. However, the obtained product contained impurities of unreacted CaO and excess C powders. Combined with, alloy precursor and non-oxygen raw materials will help improve luminescence performance of  $\text{CaSiN:Eu}^{2+}$  series nitride phosphors.

In this paper, a high performance  $\text{CaSiN:Eu}^{2+}$  red phosphors, using nano- $\text{EuB}_6$  as raw materials, were obtained by alloy precursor normal pressure nitridation. The above red phosphor exhibits an enhanced red emission and improved thermal stability, which permits it to be superior to the common used  $\text{CaSiN:Eu}^{2+}$  phosphors using  $\text{Eu}_2\text{O}_3$  and EuN as raw materials. The possible performance of the red phosphor in W-LED was also investigated.

## 2. Experimental

### 2.1. Sample Preparation

The powder samples were synthesized by the alloy precursor normal pressure nitridation method in a high temperature tubular furnace with the raw materials of CaSi alloy, AlN (99.5%),  $\text{Eu}_2\text{O}_3$  (99.99%), EuN (99.9%) and nano- $\text{EuB}_6$ .  $\text{EuB}_6$  is a typical semimetal material, Eu atoms are centered as an octahedron composed of six rigidly bound lighter atoms of boron. Thus, it has rich structure and excellent physical and chemical properties [29,30]. The energy bands of the  $\text{EuB}_6$  can be considered to be formed by orbital interactions between  $\text{Eu}^{2+}$  and  $\text{B}_6^{2-}$  clusters. Synthesized nano- $\text{EuB}_6$  was reported method by the Bao et al. [31].  $\text{Eu}_2\text{O}_3$  (99.99%) and  $\text{NaBH}_4$  (99.0%) mixed in an agate mortar for 30 min. Then the mixtures were put into a quartz tube and placed in the resistance furnace at a reaction temperature in the range from  $1150^\circ\text{C}$  to  $1200^\circ\text{C}$  for 2 h. Therein CaSi alloy is sintered by reactants Ca (99.5%), Si (99.999%) through arc melting process in Ar gas. The resulting mixtures that using  $\text{Eu}_2\text{O}_3$  and EuN as raw materials were heated at  $1550^\circ\text{C}$  for 4 h under a  $200\text{ mL min}^{-1}$   $\text{N}_2$  (99.999%) and  $20\text{ mL min}^{-1}$   $\text{H}_2$  (99.999%) reducing atmosphere with a constant flow rate  $100\text{ mL/min}$  while that using nano- $\text{EuB}_6$  were heated at  $1550^\circ\text{C}$  for 4 h under a  $200\text{ mL min}^{-1}$   $\text{N}_2$  (99.999%). Finally, the samples were cooled to room temperature in the furnace and ground again for the following characterization.

### 2.2. Measurements and Characterization

The microstructure and chemical composition of powders were imaged and measured by using a scanning electron microscopy (SEM, Hitachi S-3400N, Hitachi High-Tech Fielding Corporation, Tokyo, Japan) and X-ray energy dispersive spectrometer (EDS, Hitachi, Tokyo, Japan) equipment. The crystal structure was determined via X-ray powder diffraction (XRD, Philip PW1830 with  $\text{Cu K}\alpha$  radiation operating at 30 kV and 30 mA, Amsterdam, The Netherlands) at room temperature. The X-ray photoelectron spectroscopy (XPS) spectra were carried out with the X-ray photoelectron spectrometer (ESCALAB 250, Thermo Fisher Scientific, Loughborough, UK) using  $\text{Al K}\alpha_1$  radiation at 15 kV and 10 mA. The emission spectra were measured by a Hitachi F4600 fluorescence spectrophotometer

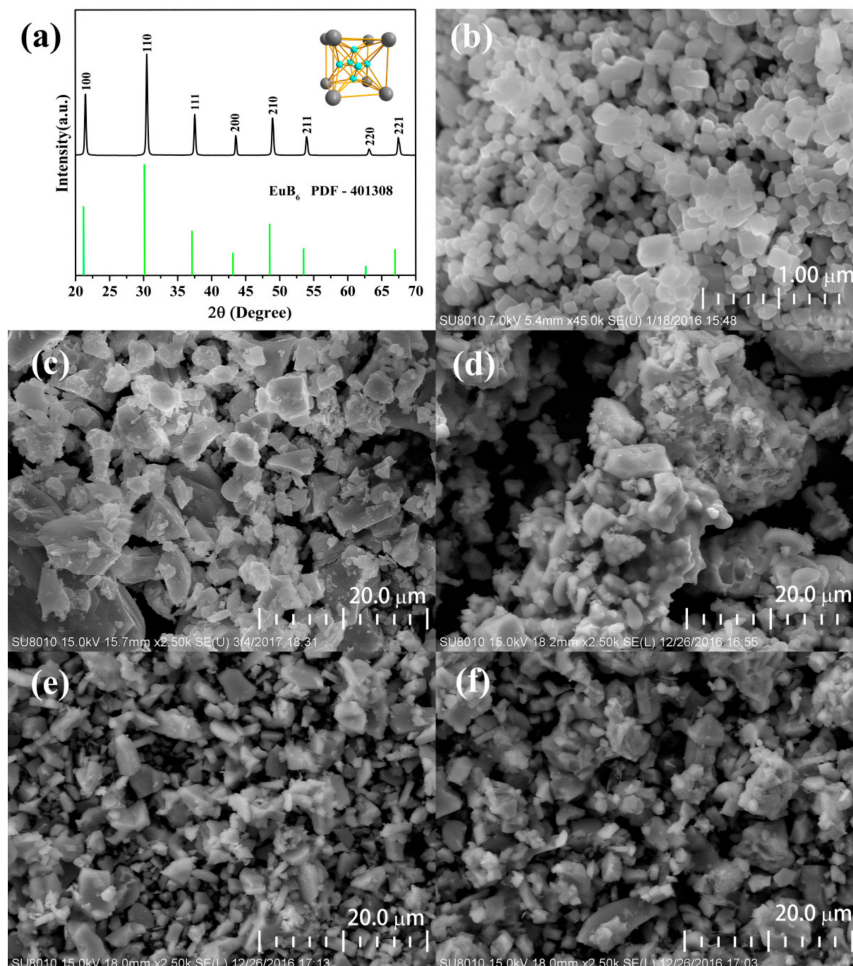
(Hitachi, Tokyo, Japan). The temperature-dependent PL spectra were also carried out on Hitachi F-7000 spectrometer (Hitachi, Tokyo, Japan) with an external heater.

A white LED was fabricated by combining a blue-LED chip (455 nm) with commercial green phosphor G3537, the as-synthesized  $\text{CASN:Eu}^{2+}$ . The optical properties of the fabricated W-LEDs were measured using sphere spectroradiometer system (LHS-1000, Everfine Co., Hangzhou, China). The working bias voltage and current of LEDs are respectively 3.4 V and 20 mA. All the measurements were conducted at room temperature unless mentioned specially.

### 3. Results and Discussion

#### 3.1. Structure Characterization

The XRD pattern and the crystal structure of the used nano- $\text{EuB}_6$  were shown in Figure 1a. The morphologies of nano- $\text{EuB}_6$ , CaSi alloy powder and the as-synthesized samples  $\text{CASN:Eu}^{2+}@Eu_2O_3$ ,  $\text{CASN:Eu}^{2+}@EuN$ , as well as  $\text{CASN:Eu}^{2+}@EuB_6$  were observed by the SEM image in Figure 1b–f. The central particle size of the used nano- $\text{EuB}_6$  is around 200–300 nm. One can find that there exists an obvious agglomeration in  $\text{CASN:Eu}^{2+}@Eu_2O_3$ , whose particles is relatively bigger and irregular than those of  $\text{CASN:Eu}^{2+}@EuN$  and  $\text{CASN:Eu}^{2+}@EuB_6$ .



**Figure 1.** XRD patterns of (a) nano- $\text{EuB}_6$  and the SEM images of (b) nano- $\text{EuB}_6$ ; (c) CaSi alloys; (d)  $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@Eu_2O_3$ ; (e)  $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuN$ ; and (f)  $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuB_6$ .

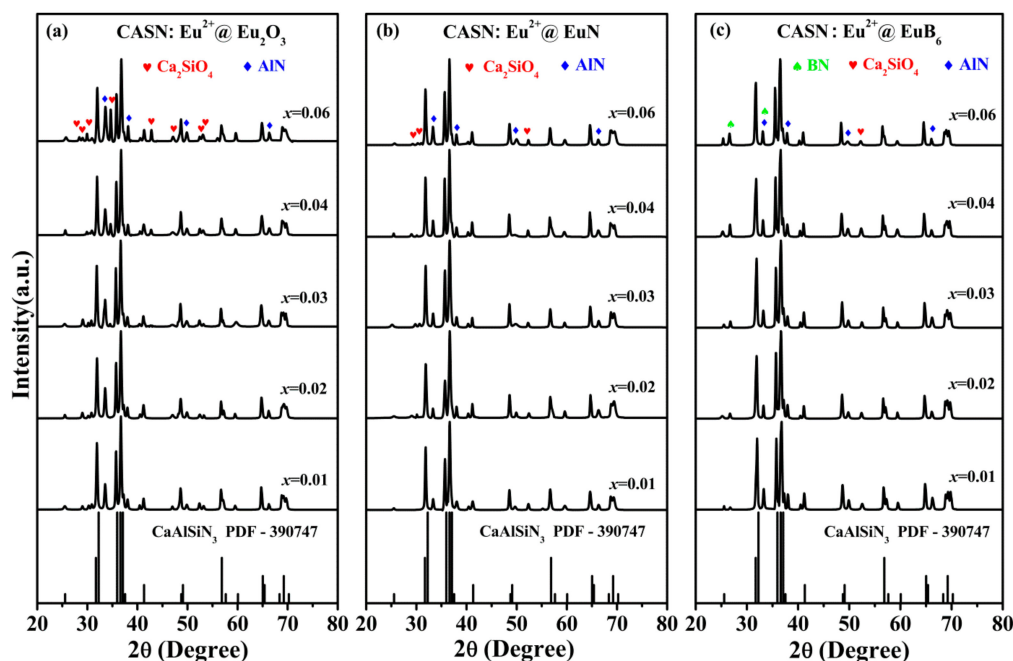
The EDS analytical data of CaSi alloys,  $\text{CASN:Eu}^{2+}@Eu_2O_3$ ,  $\text{CASN:Eu}^{2+}@EuN$  and  $\text{CASN:Eu}^{2+}@EuB_6$  were listed in Table 1. One can find that there exists a small amount of oxygen

in CaSi alloys and it cannot be avoided effectively. The EDS analysis reveals that CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> contains least oxygen while the maximum oxygen content in CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>. The possible explanation of this phenomenon is that Eu<sub>2</sub>O<sub>3</sub> is not fully reduced by local substances during sintering operations. It should be mentioned that the powders synthesized by EuN as the raw material are easier to be oxidized due to its high activity. Comparatively, the EuB<sub>6</sub> has the properties of physically and chemically stable, which prevents it from oxidation. The small amount of oxygen impurities in CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> are also attributed to the CaSi alloy, which could be reduced under a reducing atmosphere.

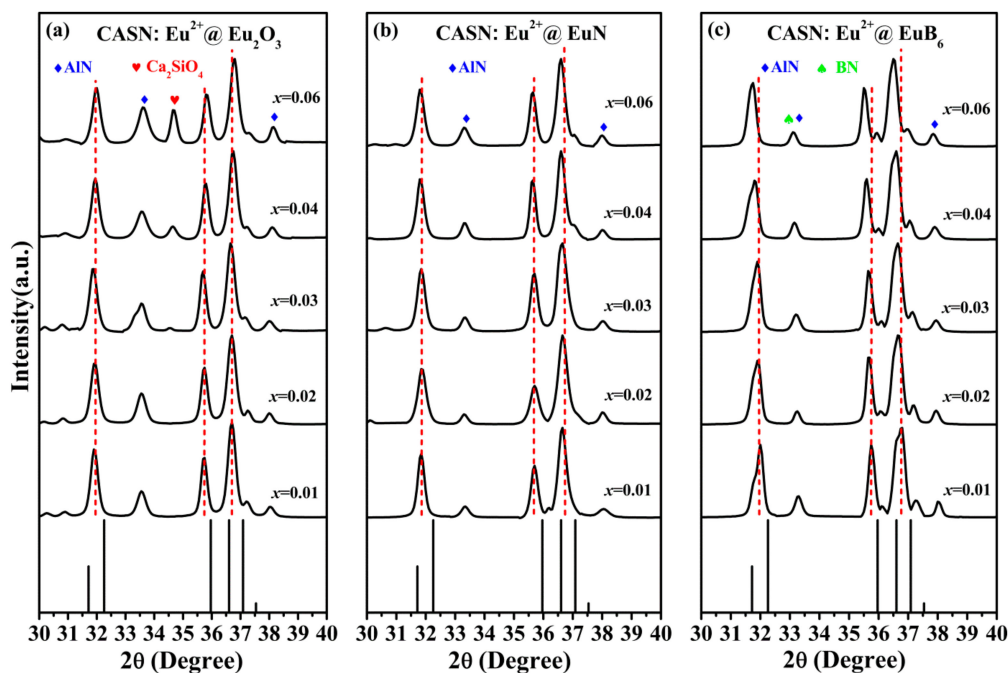
**Table 1.** EDS analytical data of CaSi alloys, Ca<sub>0.94</sub>AlSiN<sub>3</sub>:0.06Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>, Ca<sub>0.94</sub>AlSiN<sub>3</sub>:0.06Eu<sup>2+</sup>@EuN and Ca<sub>0.94</sub>AlSiN<sub>3</sub>:0.06Eu<sup>2+</sup>@EuB<sub>6</sub>.

| Element (wt %)  | B    | N     | O    | Al    | Si    | Ca    | Eu   |
|---|------|-------|------|-------|-------|-------|------|
| CaSi alloys   | —    | —     | 4.28 | —     | 59.39 | 36.33 | —    |
| Ca <sub>0.94</sub> AlSiN <sub>3</sub> :0.06Eu <sup>2+</sup> @Eu <sub>2</sub> O <sub>3</sub> | —    | 21.52 | 6.19 | 18.05 | 28.53 | 22.53 | 3.26 |
| Ca <sub>0.94</sub> AlSiN <sub>3</sub> :0.06Eu <sup>2+</sup> @EuN                            | —    | 36.33 | 2.78 | 18.04 | 23.83 | 15.76 | 3.25 |
| Ca <sub>0.94</sub> AlSiN <sub>3</sub> :0.06Eu <sup>2+</sup> @EuB <sub>6</sub>               | 5.17 | 25.56 | 1.95 | 18.27 | 26.49 | 19.32 | 3.27 |

The XRD patterns of three series CASN:Eu<sup>2+</sup> ( $x = 0.01, 0.02, 0.03, 0.04, 0.06$ ) phosphors using Eu<sub>2</sub>O<sub>3</sub>, EuN and EuB<sub>6</sub> as raw materials, labeled as CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>, CASN:Eu<sup>2+</sup>@EuN as well as CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> respectively, are shown in Figure 2 the standard XRD pattern of CaAlSiN<sub>3</sub> (PDF-390747) is also shown for comparison. As illustrated in Figure 2, the diffraction peaks are predominantly identified as CaAlSiN<sub>3</sub> phase and crystallize in the orthorhombic space group Ccm2<sub>1</sub>. It should be noted that the impurity phases, Ca<sub>2</sub>SiO<sub>4</sub> (PDF-110585) and AlN (PDF-871054) in CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub> and CASN:Eu<sup>2+</sup>@EuN as well as an extra phase BN (PDF-090012) in CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> are also identified, as shown in Figure 2a–c. Since the synthesis conditions of CASN:Eu<sup>2+</sup> phosphors need a high requirement for installations, the impurity phases are unavoidable during the sinter process. In our work, the impurity phase Ca<sub>2</sub>SiO<sub>4</sub> emerged during the preparation of CaSi alloy due to the oxidized process and it is expected to increase with the appearance of a rich oxygen source Eu<sub>2</sub>O<sub>3</sub>, which is confirmed by the more intense peak intensity in CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub> than that in CASN:Eu<sup>2+</sup>@EuN and CASN:Eu<sup>2+</sup>@EuB<sub>6</sub>. The above result is also consistent with the ratios of N/O in different samples that measured by EDS (see Table 1). For the impurity phase AlN, its precise stoichiometric ratio in the reaction can hardly be determined due to its low solubility in CaAlSiN<sub>3</sub>, which results in the redundant AlN [32,33]. It can be found from Figure 3 that the main diffraction peaks of CaAlSiN<sub>3</sub> in the range of 30–40° shift to a low degree with the increase of Eu<sup>2+</sup> ion concentration in CASN:Eu<sup>2+</sup>@EuB<sub>6</sub>, which could be ascribed to be the substitution of larger B<sup>2-</sup> (1.40 Å, CN = 4) for smaller N<sup>3-</sup> (1.32 Å, CN = 4) [17]. In CASN:Eu<sup>2+</sup>@EuB<sub>6</sub>, the diffraction peaks at 2θ = 33.5° is superposed by AlN and BN, which are formed within the reaction between B and N<sub>2</sub> (or AlN).



**Figure 2.** XRD patterns of three nitride red phosphors using different raw materials (a) CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>; (b) CASN:Eu<sup>2+</sup>@EuN and (c) CASN:Eu<sup>2+</sup>@EuB<sub>6</sub>.

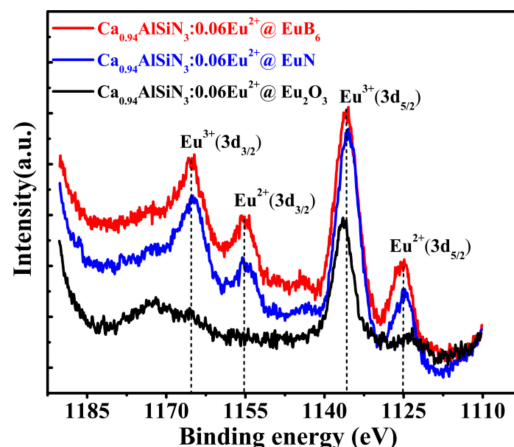


**Figure 3.** The major XRD patterns of three nitride red phosphors in the range of 30–40°; (a) CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>; (b) CASN:Eu<sup>2+</sup>@EuN and (c) CASN:Eu<sup>2+</sup>@EuB<sub>6</sub>.

### 3.2. XPS Analysis

The XPS measurement was conducted to study the local valence state of each element. The XPS spectra of Eu<sub>3d</sub> in CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub> (black line), CASN:Eu<sup>2+</sup>@EuN (blue line), as well as CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> (red line) were shown in Figure 4. According to the certain references [34,35], the bands peaking at 1165.27 eV and 1135.86 eV in Eu<sub>3d</sub> XPS spectra correspond to Eu<sup>3+</sup>(3d<sub>3/2</sub>) and Eu<sup>3+</sup>(3d<sub>5/2</sub>) respectively, while that peaking at 1155.22 eV and 1125.02 eV are attributed to Eu<sup>2+</sup>(3d<sub>3/2</sub>)

and  $\text{Eu}^{2+}(3d_{5/2})$ . In the samples of  $\text{CASN:Eu}^{2+}@EuN$  and  $\text{CASN:Eu}^{2+}@EuB_6$ , there exist the bands of  $\text{Eu}^{3+}(3d_{3/2})$ ,  $\text{Eu}^{2+}(3d_{3/2})$ ,  $\text{Eu}^{3+}(3d_{5/2})$ ,  $\text{Eu}^{2+}(3d_{5/2})$ , while in  $\text{CASN:Eu}^{2+}@Eu_2O_3$ , the bands of  $\text{Eu}^{3+}(3d_{5/2})$  dominate the spectrum. Comparative result confirms that the peak intensity ratio of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  are identical with its content ratio in  $EuN$  and  $EuB_6$  doped (see Table 2). The observation shows that  $\text{Eu}^{2+}$  content in  $\text{CASN:Eu}^{2+}@EuN$  or  $\text{CASN:Eu}^{2+}@EuB_6$  is nearly the same and both of them are higher than that in  $\text{CASN:Eu}^{2+}@Eu_2O_3$ .

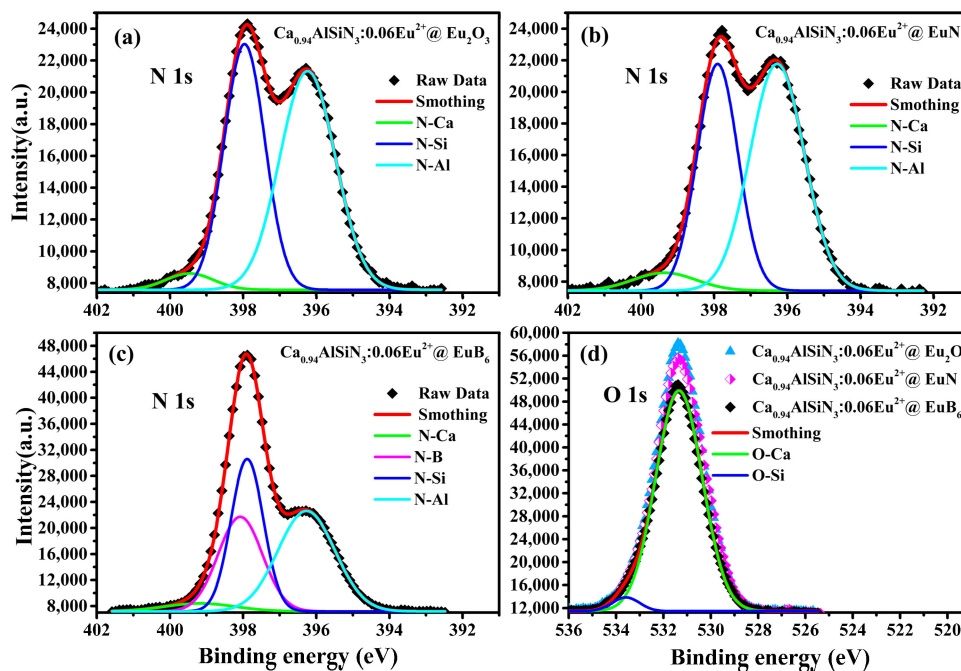


**Figure 4.** The XPS spectra of  $\text{Eu}_{3d}$  in  $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@Eu_2O_3$  (black line),  $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuN$  (blue line) and  $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuB_6$  (red line).

**Table 2.** Intensity ratios of  $\text{Eu}^{2+}/\text{Eu}^{3+}$  in  $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@Eu_2O_3$ ,  $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuN$  and  $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuB_6$ .

| XPS Measurements  | Intensity of $\text{Eu}^{2+}$ | Intensity of $\text{Eu}^{3+}$ | $\text{Eu}^{2+}/\text{Eu}^{3+}$ |
|---|-------------------------------|-------------------------------|---------------------------------|
| $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuN(3d_{3/2})$   | 0.8847                        | 0.9333                        | 9.48/10                         |
| $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuN(3d_{5/2})$   | 0.8596                        | 0.9854                        | 8.72/10                         |
| $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuB_6(3d_{3/2})$ | 0.9166                        | 0.9633                        | 9.52/10                         |
| $\text{Ca}_{0.94}\text{AlSiN}_3:0.06\text{Eu}^{2+}@EuB_6(3d_{5/2})$ | 0.8817                        | 1.0000                        | 8.82/10                         |

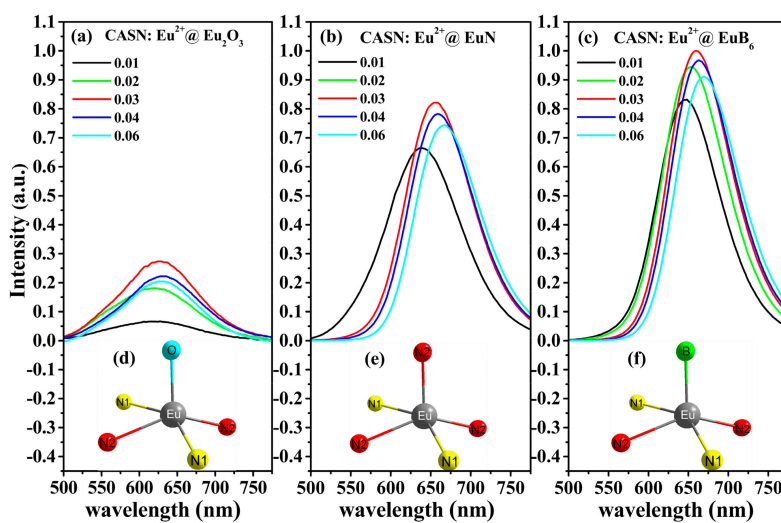
Figure 5 shows the XPS spectra of  $\text{N}_{1s}$  and  $\text{O}_{1s}$  in  $\text{CASN:Eu}^{2+}$  samples series. The  $\text{N}_{1s}$  spectra, it can also be deconvoluted into two peaks: N–Ca (green line), N–Si (blue line) and N–Al (Cyan line) bonds. The content of  $\text{N}_{1s}$  that corresponds to N–Si bond in  $\text{CASN:Eu}^{2+}@EuB_6$  is much higher than that in  $\text{CASN:Eu}^{2+}@Eu_2O_3$  and  $\text{CASN:Eu}^{2+}@EuN$  at the same Eu doping level. It was reported that the binding energy of  $\text{N}_{1s}$  that correspond to N–B (magenta line) bond was around 397.6–398.5 eV [36,37]. One can find from the XRD data that there exists the impurity phase of BN in  $\text{CASN:Eu}^{2+}@EuB_6$  sample. Therefore, it can be concluded that the peak intensity at the lower binding energy is the combined result of N–Si and N–B bonds. For the  $\text{O}_{1s}$  spectra can be deconvoluted into two peaks: O–Si (blue line) and O–Ca (green line) bonds. One can find that the peak intensity of the lower binding energy, which corresponds to O–Ca bond, has the minimum in  $\text{CASN:Eu}^{2+}@EuB_6$  while has the maximum in  $\text{CASN:Eu}^{2+}@Eu_2O_3$ . It can be concluded from the XRD data that the existence of the impurity phase of  $\text{CaSiO}_4$  is the main factor for the formation of O–Si and O–Ca bonds. Additionally, it can be found from the EDS results that oxygen content in  $\text{CASN:Eu}^{2+}@EuB_6$  was significantly less than that in  $\text{CASN:Eu}^{2+}@Eu_2O_3$  and  $\text{CASN:Eu}^{2+}@EuN$ .



**Figure 5.** The XPS spectra of O<sub>1s</sub> and N<sub>1s</sub> Ca<sub>0.94</sub>AlSiN<sub>3</sub>:0.06Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>, Ca<sub>0.94</sub>AlSiN<sub>3</sub>:0.06Eu<sup>2+</sup>@EuN and Ca<sub>0.94</sub>AlSiN<sub>3</sub>:0.06Eu<sup>2+</sup>@EuB<sub>6</sub>.

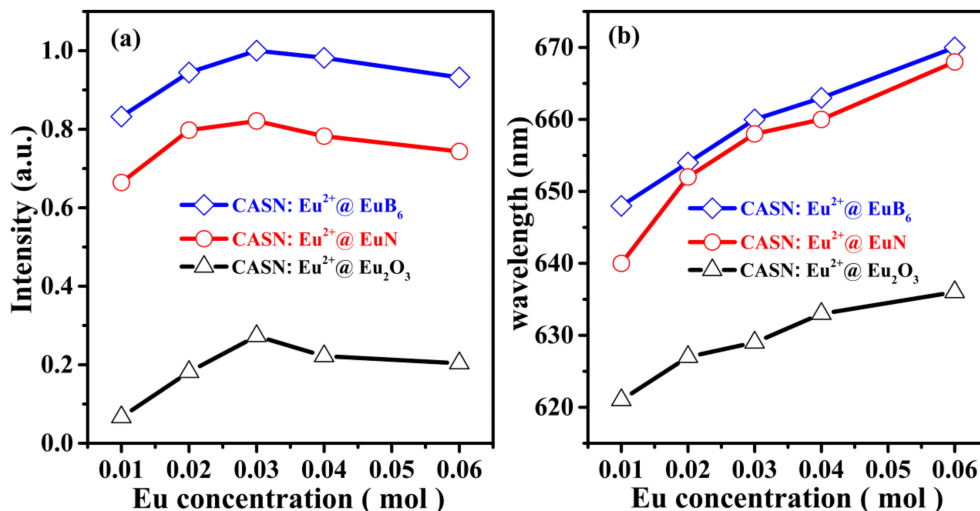
### 3.3. Photoluminescence Properties

The emission spectra of three groups of CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>, CASN:Eu<sup>2+</sup>@EuN as well as CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> ( $x = 0.01, 0.02, 0.03, 0.04, 0.06$ ) phosphors under 460 nm blue light excitation are shown in Figure 6. Upon the introduction of Eu<sup>2+</sup> ion, the emission band attributed to the  $5d \rightarrow 4f$  transition of Eu<sup>2+</sup> ion dominates the spectra in all series of samples. One can find from Figure 6a–c that the emission intensity of Eu<sup>2+</sup> ion in each group reaches its maximum value at  $x = 0.03$ , beyond which it starts to decrease due to the concentration quenching among Eu<sup>2+</sup> ions. It should be noted that the emission intensity of Eu<sup>2+</sup> ion in CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> is stronger than that in CASN:Eu<sup>2+</sup>@EuN and CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>.



**Figure 6.** Photoluminescence spectra and crystallographic environments around Eu<sup>2+</sup> ions of three series of nitride red phosphors using different raw materials (a) CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>; (b) CASN:Eu<sup>2+</sup>@EuN; (c) CASN:Eu<sup>2+</sup>@EuB<sub>6</sub>; (d) EuN<sub>2</sub><sup>I</sup>N<sub>2</sub><sup>II</sup>O; (e) EuN<sub>2</sub><sup>I</sup>N<sub>3</sub><sup>II</sup> and (f) EuN<sub>2</sub><sup>I</sup>N<sub>2</sub><sup>II</sup>B phosphors with various content  $x$  ( $x = 0.01, 0.02, 0.03, 0.04, 0.06$ ).

Under 460 nm blue light excitation, the emission peaks of CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub> fall in the scope of 621~636 nm while that of CASN:Eu<sup>2+</sup>@EuN as well as CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> are in 640~668 nm, 648~670 nm, respectively. At the same Eu<sup>2+</sup> doping concentration, the emission wavelength in CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> series is longer than that in CASN:Eu<sup>2+</sup>@EuN (as shown in Figure 7a,b).



**Figure 7.** Dependence of emission intensity (a) and peak position (b) of CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub> (black line), CASN:Eu<sup>2+</sup>@EuN (blue line) and CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> (red line) phosphors with various Eu<sup>2+</sup> concentration ( $x = 0.01, 0.02, 0.03, 0.04, 0.06$ ).

The XPS spectra reveal that Eu<sup>2+</sup> content in both CASN:Eu<sup>2+</sup>@EuN and CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> is higher than that in CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub>. The amounts of O–Si, O–Ca bonds will decline accompanied by the increase of N–Si bond with the decrease of oxygen content in host materials, as a result, it affects the crystal field, which results in the split of Eu<sup>2+</sup> energy levels. The position of the 5d emission band of the Eu<sup>2+</sup> ions at lower energy (longer wavelength) is attributed to the influence of highly covalent bonding of Eu–X (X = N, B, O) and high crystal field strength. The reduction of crystal field strength around the Eu<sup>2+</sup> ion in CASN:Eu<sup>2+</sup>@Eu<sub>2</sub>O<sub>3</sub> leads to a blue shift. However, under the influence of crystal field, the emission spectra have a larger red shift in CASN:Eu<sup>2+</sup>@EuN and CASN:Eu<sup>2+</sup>@EuB<sub>6</sub>. This is caused by the shrinkage of 5d → 4f energy level spacing [38].

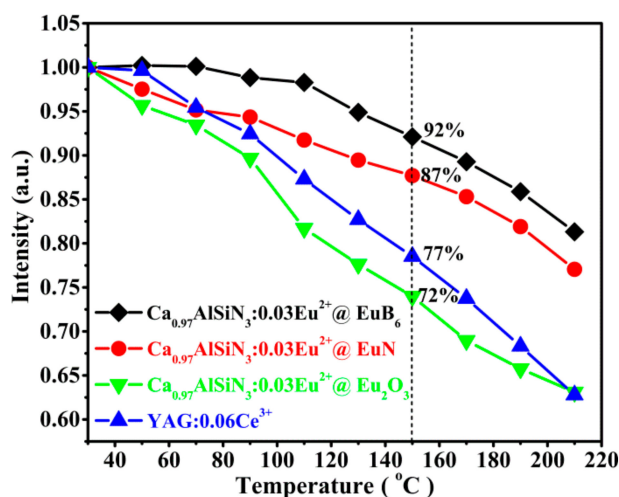
Particularly, in the series of CASN:Eu<sup>2+</sup>@EuB<sub>6</sub>, with B<sup>2−</sup> ions incorporating into the host lattice of CaAlSiN<sub>3</sub>, they substitute N<sup>3−</sup> and O<sup>2−</sup> ions through a pattern of EuN<sub>2</sub><sup>I</sup>N<sub>3</sub><sup>II</sup> → EuN<sub>2</sub><sup>I</sup>N<sub>2</sub><sup>II</sup>B (see Figure 6f) [39] then, a red shift in the spectrum was expected due to the changed crystal strength. Moreover, the Eu–N bond length critically affects the emission wavelength of nitride phosphors. Therefore, we believe that according to the above schematic pattern the length of the Eu–B bonds is longer than that of the Eu–N bonds (see Figure 6e,f). In addition, the metal cation ratio in CaAlSiN<sub>3</sub> is Ca:Al:Si = 1:1:1, in which Ca and Al/Si occupied on the 4a and 8b sites in the space group of Ccm2<sub>1</sub>, respectively [25,32]. In the series of CASN:Eu<sup>2+</sup>@EuB<sub>6</sub>, the decrease of oxygen content can prevent the formation of Ca<sub>2</sub>SiO<sub>4</sub> and increase the content of occupation Ca ions, which can also lead to the improvement of emission intensity. Since the three series of samples have the same Eu<sup>2+</sup> doping level thus the higher luminescence performance of CASN:Eu<sup>2+</sup>@EuB<sub>6</sub> indicates that Eu<sup>2+</sup> ions content in the host lattice has changed the crystal environment and the site occupancy.

### 3.4. Thermal Stability Analysis

A stable emission intensity at the elevated temperature, typically at 150 °C or even higher for high-power application is a basic requirement for phosphors converted W-LEDs thus the phosphors must have small thermal quenching to maintain the long lifetime of LED devices. In order to



evaluate the influence of the temperature on the luminescence, the temperature-dependent PL intensities of the as-prepared  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{Eu}_2\text{O}_3$ ,  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{EuN}$  as well as  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{EuB}_6$  were given in Figure 8. The temperature-dependent PL intensities of  $\text{YAG}:0.06\text{Ce}^{3+}$  phosphor were also shown for comparison. It can be easily observed that all the above four phosphors exhibit thermal quenching in different degrees with temperature increasing from 30 °C to 210 °C. In addition, one can find that as the temperature increased to 150 °C, the emission intensity declined to 72%, 87%, 92% and 77% of their initial values at room temperature for  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{Eu}_2\text{O}_3$ ,  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{EuN}$ ,  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{EuB}_6$  as well as  $\text{YAG}:0.06\text{Ce}^{3+}$ , respectively.

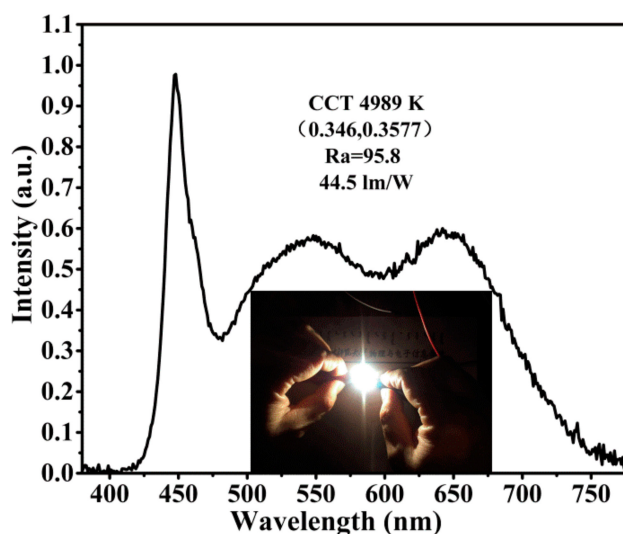


**Figure 8.** Temperature-dependent emission intensities of  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{Eu}_2\text{O}_3$  (green line),  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{EuN}$  (red line),  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{EuB}_6$  (black line) and  $\text{YAG}:0.06\text{Ce}^{3+}$  (blue line) phosphors.

It is obvious that  $\text{CaSiN}_3:\text{Eu}^{2+}@ \text{EuB}_6$  has a preferable thermal stability than others. The increased thermal stability is attributable to the partial substitution of Eu–O (Eu–N) bonds by more covalent Eu–B ones that leads to a higher structural rigidity, which has already been observed in carbon-doped nitride phosphors [40–42]. Therefore, using nano- $\text{EuB}_6$  as a raw material in nitride luminescence materials can improve the luminescence performance as well as the thermal stability.

### 3.5. The Fabrication of W-LEDs Device

To demonstrate the potential application of the as-synthesized  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{EuB}_6$  red nitrides phosphor, a prototype of W-LEDs was fabricated by combining a 455 nm blue LED chip with a mixture of commercial green phosphor G3537 (produced by Dalian Luming) and the as-synthesized red phosphor  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{EuB}_6$ . The normalized photoluminescence (PL) spectrum of the as-fabricated W-LEDs is shown in Figure 9. The corresponding CRI, CCT, luminous efficiency and CIE chromaticity coordinates were determined to be 95.8, 4989 K, 44.5 lm/W and (0.3460, 0.3577), respectively. The value of CRI is higher than that of traditional W-LED production made by combining yellow phosphor  $\text{YAG}:\text{Ce}^{3+}$  with blue LED chip ( $R_a \approx 75$ ). The W-LED packaging results indicate that the as-synthesized  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@ \text{EuB}_6$  is a potential candidate as a red phosphor for W-LEDs based on blue LEDs.



**Figure 9.** The normalized PL spectrum of a W-LED using a blue-LED chip (455 nm) and G3537 and  $\text{Ca}_{0.97}\text{AlSiN}_3:0.03\text{Eu}^{2+}@\text{EuB}_6$  phosphors.

#### 4. Conclusions

In this paper, three series of  $\text{CASN:Eu}^{2+}$  red nitride phosphors, using  $\text{Eu}_2\text{O}_3$ ,  $\text{EuN}$  and  $\text{EuB}_6$  as raw materials, were successfully synthesized by the alloy precursor normal pressure nitridation. The morphologies, crystal phases, compositions, XPS spectra as well as luminescence properties were investigated in detail. Interrelated Analysis of XPS indicates that the  $\text{Eu}^{2+}$  content in  $\text{CASN:Eu}^{2+}@\text{EuB}_6$  is significantly higher than in  $\text{CASN:Eu}^{2+}@\text{Eu}_2\text{O}_3$ , thus it causes a stronger emission intensity of  $\text{CASN:Eu}^{2+}@\text{EuB}_6$  than others. Furthermore,  $\text{CASN:Eu}^{2+}@\text{EuB}_6$  has a preferable thermal stability is attributable to the partial substitution of  $\text{Eu-O}$  ( $\text{Eu-N}$ ) bonds by more covalent  $\text{Eu-B}$  ones that leads to a higher structural rigidity. Consequently, nano- $\text{EuB}_6$  doped red nitride phosphor has the potential for application in high-power pc-LEDs and using nano- $\text{EuB}_6$  as raw material by the alloy precursor normal pressure nitridation method possesses the high advantage of relative low reaction temperature, cheap raw materials and simple processing.

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