Correlation of Structure, Tunable Colors, and Lifetimes of (Sr, Ca, Ba)Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ Phosphors

Qidi Xie, Bowen Li, Xin He, Mei Zhang, Yan Chen and Qingguang Zeng

School of Applied Physics and Materials, Wuyi University, Jiangmen 529020, China; qidixie@163.com (Q.X.); libowenliboyuan@126.com (B.L.); ychen08@163.com (Y.C.); zengqg1979@126.com (Q.Z.)

School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

* Correspondence: hexin@mail.wyu.edu.cn (X.H.); zmjenny@163.com (M.Z.)

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Abstract: (Sr, Ca, Ba)Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors were prepared via a high temperature solid-state reaction method. The correlation of phase structure, optical properties and lifetimes of the phosphors are investigated in this work. For the (Sr, Ca)Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors, the different phase formation from monoclinic SrAl$_2$O$_4$ phase to hexagonal SrAl$_2$O$_4$ phase to monoclinic CaAl$_2$O$_4$ phase was observed when the Ca content increased. The emission color of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors varied from green to blue. For the (Sr, Ba)Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors, different phase formation from the monoclinic SrAl$_2$O$_4$ phase to the hexagonal BaAl$_2$O$_4$ phase was observed, along with a shift of emission wavelength from 520 nm to 500 nm. More interestingly, the decay time of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ changed due to the different phase formations. Lifetime can be dramatically shortened by the substitution of Sr$^{2+}$ with Ba$^{2+}$ cations, resulting in improving the performance of the alternating current light emitting diode (AC-LED). Finally, intense LEDs are successfully obtained by combining these phosphors with Ga(In)N near UV chips.

Keywords: phosphors; solid solution; average lifetime; AC-LEDs; photoluminescence

1. Introduction

AC-LED is a new type of device that can be directly driven by the alternating current of city power. It has experienced rapid development and is widely applied in indoor and outdoor lighting due to its long life, low price, high efficiency, etc. [1–4]. However, the vital defect of the AC-LED is the flickering effect, with a time gap of 5–20 ms [4–6], resulting in visual fatigue and health hazards. There have been several solutions to reduce flashing in AC-LED, such as using a converter-free AC-LED driver, increasing drive frequency etc. However, these solutions suffer from low power efficiency or large size. Fortunately, the use of long afterglow phosphors is considered to be a promising method to compensate for the time gap and reduce the flickering effect. Long afterglow phosphors, such as SrSi$_2$O$_5$N$_2$:Eu$^{2+}$, Mn$^{2+}$ [2], SrAl$_2$O$_4$:Eu$^{2+}$, Ce$^{3+}$, Li$^+$ [5], and SrAl$_2$O$_4$:Eu$^{2+}$, and RE$^{3+}$ (RE = Y, Dy) have been studied and applied to AC-LEDs [4,7].

SrAl$_2$O$_4$:Eu$^{2+}$ is one of green phosphors for UVLEDs. When it is co-doped with RE$^{3+}$ (RE = Dy, Y, Nd and Ho), SrAl$_2$O$_4$:Eu$^{2+}$, RE$^{3+}$ can store electrons to achieve long and persistent luminescence. However, the afterglow time of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ is too long to fulfill the requirement of AC-LED. In our previous research, we shortened the average lifetime of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors from 845.86 ms to 428.83 ms by changing the amount of SrCl$_2$ flux. Moreover, MAI$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ (M = Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) phosphors with different cations also have different defect levels and afterglow times [7–13]. Therefore, the substitution of Sr$^{2+}$ by Ca$^{2+}$ or Ba$^{2+}$ ions in SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors is expected to tune the afterglow time. Furthermore, the emission and excitation spectra of Eu$^{2+}$ ions can also be modified by the different radius of Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$ ions and crystal structures [13–16].
This paper aims to improve the emission color and the average lifetime of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors by partially substituting Sr$^{2+}$ with Ca$^{2+}$ or Ba$^{2+}$ ions. The effect and correlation of Ca$^{2+}$ or Ba$^{2+}$ ions substitution on the obtained phases, optical properties, and decay times of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors are systematically investigated. The electroluminescent properties of the as-fabricated LEDs based on UV-chips and MA$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ (M = Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) phosphors are also investigated.

2. Experimental Procedure

Sr$_{0.90-x}$Ca$_3$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ and Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ samples ($x$ or $y$ = 0.00, 0.15, 0.30, 0.45, 0.60, 0.75, 0.90) were prepared by a high temperature solid-state reaction method. The raw materials CaCO$_3$ (99.99%), SrCO$_3$ (99.99%), BaCO$_3$ (99.99%), Al$_2$O$_3$ (99.99%), Eu$_2$O$_3$ (99.99%), Dy$_2$O$_3$ (99.99%) and H$_3$BO$_3$ (99.99%) were weighted stoichiometrically. The original materials were mixed into an agate mortar and placed into a small alumina crucible. Then, the mixtures were put into a tubular furnace and heated to 900 °C for 2 h. Being reground, they were heated to 1400 °C for 4 h under a reductive atmosphere from burning activated carbon. Finally, the samples were cooled to room temperature, resulting in Sr$_{0.90-x}$Ca$_3$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$, and Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ compounds.

The structure of Sr$_{0.90-x}$Ca$_3$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$, and Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors were explored by X-ray powder diffraction (XRD) using a Diffractometer (X’Pert PRO, PANalytical, Almelo, Netherlands) with Cu K$_{α}$ radiation at 40 kV and 20 mA. The data were collected in the 2θ range of 10° to 80°. The photoluminescence (PL) spectra and decay curves were performed by a spectrofluorometer (F-4600, Hitachi, Tokyo, Japan) equipped with a 150W Xe lamp as the light source.

The phosphors were pre-coated on near-UV Ga(In)N chips with 365 and 395 nm emission, respectively. The emission spectra and parameters of the as-fabricated LEDs were measured by the LED spectrophotocolorimeter (PMS 50, Everfine Co., Ltd., Hangzhou, China) with an integrating sphere of 50 cm diameter. The normal forward-bias current was 20 mA. All measurements were conducted at room temperature.

3. Results and Discussion

3.1. X-ray Diffraction Analysis

XRD patterns of Sr$_{0.90-x}$Ca$_3$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ ($x$ = 0.00–0.90) phosphors with various $x$ values are depicted in Figure 1a. The patterns are compared with the JCPDS standard cards of possible phases and marked with different symbols. For $x$(Ca$^{2+}$) = 0.00, the diffraction peaks are well matched with the monoclinic SrAl$_2$O$_4$ (MP-SrAl$_2$O$_4$, JCPDS card No. 74-0794), and minor content of the raw material—Al$_2$O$_3$—is observed due to the incomplete reaction, which is explained by our previous work [4]. For $x$(Ca$^{2+}$) = 0.15, the dominant phase is the hexagonal SrAl$_2$O$_4$ (HP-SrAl$_2$O$_4$, JCPDS card No. 31-1336). Thus, the different phase formation from the monoclinic to the hexagonal phase happens in Sr$_{0.90-x}$Ca$_3$Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors when the substitution of Sr$^{2+}$ by Ca$^{2+}$ increases from 0.00 to 0.15. The hexagonal phase remains when $x$(Ca$^{2+}$) = 0.30. Simultaneously, the MP-SrAl$_2$O$_4$ disappears and minor content of monoclinic CaAl$_2$O$_4$ phase emerges. The monoclinic CaAl$_2$O$_4$ phase (MP-CaAl$_2$O$_4$, CPDS card No.53-0191) gradually increases with further elevating concentration of Ca$^{2+}$ from 0.45 to 0.75, accompanying with the decrease of HP-SrAl$_2$O$_4$. For $x$(Ca$^{2+}$) = 0.90, the dominant phase is MP-CaAl$_2$O$_4$. In general, as $x$(Ca$^{2+}$) varies from 0.00 to 0.90, and the obtained phases can be varied as follows: MP-SrAl$_2$O$_4$ → HP-SrAl$_2$O$_4$ → MP-CaAl$_2$O$_4$. Furthermore, it can be concluded that two different phase always coexist due to the cations substitution except for the samples with $x$(Ca$^{2+}$) = 0.00 and 0.90. The phase change is different with that of other report under different synthesized condition [13].
Unlike the substitution of Sr\(^{2+}\) by Ca\(^{2+}\) in SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) phosphors, there is only the variation from MP-SrAl\(_2\)O\(_4\) to hexagonal BaAl\(_2\)O\(_4\) phase (HP-BaAl\(_2\)O\(_4\), JCPDS card No. 17-0306) during the substitution of Sr\(^{2+}\) by Ba\(^{2+}\). The coexistence of two phases cannot be observed from the XRD data, as displayed in Figure 2b. Specifically, when \(y(\text{Ba}^{2+}) = 0.00\)–0.30, the crystal structure remains the MP-SrAl\(_2\)O\(_4\). However, as \(y(\text{Ba}^{2+}) = 0.45\), the XRD patterns are consistent with the standard HP-BaAl\(_2\)O\(_4\). It remains unchanged while \(y\) varies from 0.45 to 0.90, which stems from the small radius of Sr\(^{2+}\) compared to that of Ba\(^{2+}\) and the effect of chemical pressure of Ba\(^{2+}\) on the crystal structure. Therefore, the Sr\(_{0.90-y}\)Ba\(_y\)Al\(_2\)O\(_4\):0.05Eu\(^{2+}\), 0.05Dy\(^{3+}\) compounds can be regarded as the hexagonal BaAl\(_2\)O\(_4\) phase replaced by Sr\(^{2+}\) ions as \(y(\text{Ba}^{2+}) = 0.45\)–0.90. The different phase formation from MP-SrAl\(_2\)O\(_4\) to HP-BaAl\(_2\)O\(_4\) can be obtained when Sr\(^{2+}\) is replaced by Ba\(^{2+}\) in SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) phosphors.
Another finding is that the peaks of the Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors with varied $x$ values (Inset is the normalized emission spectra of). Excitation and emission spectra of Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors with varied $y$ values (Inset is the normalized emission spectra).

Figure 2. (a) Excitation and (b) emission spectra of Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors with varied $x$ values (Inset is the normalized emission spectra of); (c) excitation and (d) emission spectra of Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors with varied $y$ values (Inset is the normalized emission spectra).

3.2. Luminescence Properties of Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ and Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ Phosphors

Figure 2 illustrates the emission and excitation spectra of Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ and Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors with $x(y)$ ranged from 0.00 to 0.90. The excitation spectra of Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors are depicted in Figure 2a with monitoring the emission of Eu$^{2+}$ in the range of 440–510 nm. All samples present broad bands from 250 nm to 450 nm due to $4f^7\rightarrow 4f^65d^1$ transitions of Eu$^{2+}$ ions [18]. The shape of excitation bands almost remain unchanged while the intensity decreases when $x$ value ($x=0.00-0.45$) increases. However, it should be noted that excitation bands are different from those of $x<0.60$. The excitation bands of Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ ($x=0.60-0.90$) are similar and blue-shift, which is ascribed to the phase variation as discussed in XRD analysis. Figure 2b shows the emission spectra of Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors. It can be divided into three sections ($x=0.00-0.30$, $x=0.45-0.60$, $x=0.75-0.90$). Interestingly, these results are related to the phase transition. First, the luminescence intensity decreases and the emission peak shifts from 520 nm to 538 nm as $x$ varied from 0.00 to 0.30. Second, two emission peaks around 450 nm, 540 nm at $x=0.45-0.60$ are observed due to
the coexistence of heterogeneous mixtures of two structures. Finally, the emission spectrum presents a single peak around 444 nm when x value increased from 0.75 to 0.90, while the dominant phase is monoclinic CaAl₂O₄.

The emission band shifts to a shorter wavelength from 520 nm to 500 nm as phosphors have a little shift from green (0.2399, 0.5867, point M) to bluish green (0.1652, 0.4645, point A) area. The above discussion indicates that the emission color of Sr₂Al₂O₄:Eu²⁺, Dy³⁺ phosphors can be tuned by Ca²⁺ or Sr²⁺ content. For Sr₀.₉₀−₀.yBa₂Al₂O₄:0.05Eu²⁺, 0.05Dy³⁺ phosphors with varied x (or y) values are presented in Figure 3 and Table 1. These results show that the CIE color coordinates of SrAl₂O₄:Eu²⁺, Dy³⁺ phosphors can be tuned by Ca²⁺ or Sr²⁺ content. For Sr₀.₉₀−₀.yBa₂Al₂O₄:0.05Eu²⁺, 0.05Dy³⁺ phosphors, the color coordinates can be changed from green (0.2393, 0.5874, point M) to blue (0.1531, 0.0528, point A) area with x increased. In addition, the color coordinates of Sr₀.₉₀−₀.yBa₂Al₂O₄:0.05Eu²⁺, 0.05Dy³⁺ phosphors have a little shift from green (0.2399, 0.5867, point M) to bluish green (0.1652, 0.4645, point B) area. The above discussion indicates that the emission color of SrAl₂O₄:Eu²⁺, Dy³⁺ can be tuned due to the phase change of the substitution of Sr²⁺ with Ca²⁺ or Ba²⁺ ions. It is an important challenge to tune the color of phosphors for improving the color rendering index of w-LEDs [20–22].

![Figure 3. CIE chromaticity diagram of Sr₀.₉₀−₀.yCa₂Al₂O₄:0.05Eu²⁺, 0.05Dy³⁺ and Sr₀.₉₀−₀.yBa₂Al₂O₄:0.05Eu²⁺, 0.05Dy³⁺ phosphors with various x (or y) values (x, y = 0.00–0.90).](image)

**Table 1.** Color coordinates of Sr₀.₉₀−₀.yCa₂Al₂O₄:0.05Eu²⁺, 0.05Dy³⁺ and Sr₀.₉₀−₀.yBa₂Al₂O₄:0.05Eu²⁺, 0.05Dy³⁺ phosphors (x, y = 0.00–0.90).

| x (or y) Values | Sr₀.₉₀−₀.yCa₂Al₂O₄:0.05Eu²⁺, 0.05Dy³⁺ | Sr₀.₉₀−₀.yBa₂Al₂O₄:0.05Eu²⁺, 0.05Dy³⁺ |
|----------------|-----------------------------------|-----------------------------------|
|                | CIE (x, y)                        | CIE (x, y)                        |
| 0.00           | 0.2393 0.5874                     | 0.2399 0.5867                     |
| 0.15           | 0.2741 0.5754                     | 0.2251 0.5675                     |
| 0.30           | 0.3029 0.5456                     | 0.2170 0.5477                     |
| 0.45           | 0.2860 0.4986                     | 0.2258 0.4952                     |
| 0.60           | 0.2059 0.1712                     | 0.2054 0.4741                     |
| 0.75           | 0.1607 0.0729                     | 0.1823 0.4412                     |
| 0.90           | 0.1531 0.0528                     | 0.1652 0.4645                     |
3.3. Decay Characteristics

The photoluminescence decay curves of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors with varied Ca$^{2+}$ and Ba$^{2+}$ content are shown in Figure 4a,b, respectively. The figures reveal the initial luminous intensity is different when Sr$^{2+}$ is replaced by either Ca$^{2+}$ or Ba$^{2+}$ in SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$. Among these phosphors, Sr$_{0.90}$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ has the highest initial luminous intensity. The initial luminous intensity gradually decreases when the content of Ca$^{2+}$(Ba$^{2+}$) increased to 0.45. By further increasing the Ca$^{2+}$ or Ba$^{2+}$ concentration, the initial luminous intensity enhances. The variation of initial luminous intensity is consistent with the emission spectra, which can be explained by the change of crystal structure.

The average lifetimes can be obtained as follows. The detail parameters are listed in Table 2.

\[ I(t) = I_0 + Ae^{-t/\tau_1} + Be^{-t/\tau_2} + Ce^{-t/\tau_3} \]  

(1)

Figure 4. (a) Photoluminescence decay curves of Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ with various x(Ca$^{2+}$) ($\lambda_{ex} = 370$ nm $\lambda_{em} = 440-510$ nm); (b) photoluminescence decay curves of Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ with various y(Ba$^{2+}$) ($\lambda_{ex} = 370$ nm $\lambda_{em} = 495-510$ nm); (c) normalized decay and fitted curves of phosphors (Ca$_{0.90}$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$, Sr$_{0.90}$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$, Ba$_{0.90}$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$); (d) average lifetimes of Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$, and Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$.

Moreover, the decay process of all samples is composed of fast decay, medium decay and subsequent of slow decay, which is consistent with our previous report. The decay curves of Ca$_{0.90}$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$, Sr$_{0.90}$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$, and Ba$_{0.90}$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors are fitted as representatives, which are presented in Figure 4c. The decay curves are well fitted with the following triple exponential functions:
where \( t \) is the time, \( I_0 \) and \( I \) is the luminescence intensity at initial time and \( t \), respectively. \( A, B \) and \( C \) are constants. \( \tau_1, \tau_2, \) and \( \tau_3 \) are the decay time for the exponential components, respectively. The average lifetimes can be obtained as follows. The detail parameters are listed in Table 2.

\[
\tau_{average} = \frac{\int_0^\infty t \times I(t)dt}{\int_0^\infty I(t)dt}
\]

(2)

| Samples | Decay Lifetimes (ms) | | |
|---------|----------------------|--|---|
| Ca_{0.90}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} | 210.28 | 210.28 | 1410.88 | 795.11 |
| Sr_{0.90}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} | 1264.65 | 165.05 | 165.05 | 842.04 |
| Ba_{0.90}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} | 134.50 | 1502.09 | 134.50 | 219.91 |

On the basis of the Equation (2), the average lifetime (\( \tau_{average} \)) of SrAl_{2}O_{4}:Eu^{2+}, Dy^{3+} phosphors with varied Ca^{2+} and Ba^{2+} contents are determined and shown in Figure 4d, respectively. The order of the average lifetimes is Sr_{0.90}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} > Ca_{0.90}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} > Ba_{0.90}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+}. The average lifetimes of Sr_{0.90}..Ca_{x}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} phosphors vary with the change of Ca^{2+} content, and the maximum is about 1088.5 ms at \( x = 0.45 \). It could be ascribed to the complicate formation of the phase in Figure 1. Furthermore, the average lifetimes of Sr_{0.90−y}Ba_{y}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} phosphors gradually decrease with Ba^{2+} content increased due to the different phase formation and reach the shortest time of 219.91 ms at \( y = 0.90 \), demonstrating that the average lifetime or decay characteristics of SrAl_{2}O_{4}:Eu^{2+}. Dy^{3+} could be adjusted by the partial substitution of Ba^{2+}, Ca^{2+}. The results also indicate that the tuned lifetimes are more suitable for the application in AC-LEDs as the global widely utilize 50/60 Hz alternating current with a 5–20 ms dark duration.

3.4. Application of SrAl_{2}O_{4}:Eu^{2+}, Dy^{3+} Phosphors with Varied Contents of Ca^{2+} and Ba^{2+} in LEDs

Finally, phosphors converted LEDs were fabricated with silicone, near UV-chips (~365 nm, 395 nm), Sr_{0.90−x}Ca_{x}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+}, and Sr_{0.90−y}Ba_{y}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} phosphors. The phosphors account for 20% of the mass of silicone.

Figure 5 is the electroluminescence spectra of the as-fabricated LEDs based on Sr_{0.90−x}Ca_{x}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} phosphors and near UV Ga(In)N chips. In the Figure 4a, the shapes of all electroluminescence spectra in the as-fabricated LEDs are similar with the photoluminescence emission spectra of Sr_{0.90−x}Ca_{x}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} phosphors because the near UV around 365 nm of chips is completely absorbed by phosphors. Figure 5b depicts that the emission band located at 395 nm belongs to the UV-chips. And other emission bands are ascribed to Eu^{2+} emissions excited by 395 nm UV-chips. The results prove that the Sr_{0.90−x}Ca_{x}Al_{2}O_{4}:0.05Eu^{2+}, 0.05Dy^{3+} fluorescence materials can absorb the light with wavelength of 365 nm or 395 nm, and convert it into green or blue visible-light. The CIE color coordinates of as-fabricated LEDs are calculated and listed in Table 3. The inset of Figure 5 presents the chromaticity diagram of the as-fabricated LEDs based on SrAl_{2}O_{4}:Eu^{2+}, Dy^{3+} phosphors, which can be tuned from green to blue area and are similar with that of phosphors. In addition, the luminous efficiency is also systematically investigated under 20 mA forward-bias current in this work, as indicated in Figure 5c. The luminous efficiency of the as-fabricated LEDs with 395 nm is higher than in the case of 365 nm UV chips. However, for both kinds of LEDs fabricated by 365 nm and 395 nm UV-chips, the luminous efficiency decreases strongly, then increases slowly with Ca^{2+} content elevated. The maximum luminous efficiency is 11.24 lm/W for 365 nm LEDs and 35.35 lm/W for 395 nm LEDs (\( x = 0 \)).
Figure 5. Electroluminescence spectra of the as-fabricated LEDs based on UV chip and Sr$_{0.90-x}$Ca$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors under 20 mA forward-bias current (i.e., $I_F = 20$ mA). Inset is chromaticity diagram of the as-fabricated LEDs: (a) 365 nm UV chip; (b) 395 nm UV-chip; (c) Luminous efficiency of as-fabricated LEDs with different Ca$^{2+}$ content under $I_F = 20$ mA.
Table 3. Parameter of chromaticity coordinates based on $\text{Sr}_{0.90-x}\text{Ca}_x\text{Al}_2\text{O}_4:0.05\text{Eu}^{2+}, \ 0.05\text{Dy}^{3+}$ phosphors with 365 nm and 395 nm UV-Chips under 20 mA forward-bias current.

| $x$ Values | 395 UV-Chips | 365 UV-Chips |
|-----------|--------------|--------------|
|           | CIE ($x$, $y$) | CIE ($x$, $y$) |
|           | $x$          | $y$          | $x$          | $y$          |
| 0.00      | 0.2805       | 0.5527       | 0.2907       | 0.5657       |
| 0.15      | 0.3029       | 0.5005       | 0.3181       | 0.5301       |
| 0.30      | 0.3033       | 0.4120       | 0.3462       | 0.5032       |
| 0.45      | 0.2555       | 0.2402       | 0.3139       | 0.3662       |
| 0.60      | 0.2209       | 0.1497       | 0.2486       | 0.2125       |
| 0.75      | 0.1675       | 0.0669       | 0.1771       | 0.0983       |
| 0.90      | 0.1599       | 0.0572       | 0.1655       | 0.0791       |

The electroluminescence spectra of LEDs based on $\text{Sr}_{0.90-x}\text{Ba}_x\text{Al}_2\text{O}_4:0.05\text{Eu}^{2+}, \ 0.05\text{Dy}^{3+}$ phosphors are also investigated, as shown in Figure 6. Except emission peaks of the UV chip itself, all of the electroluminescence spectra of $\text{Sr}_{0.90-x}\text{Ba}_x\text{Al}_2\text{O}_4:0.05\text{Eu}^{2+}, \ 0.05\text{Dy}^{3+}$ excited by both 365 nm and 395 nm UV-chips are similar. It indicates that the $\text{Sr}_{0.90-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \ \text{Dy}^{3+}$ phosphors can absorb 365 nm or 395 nm emission from Ga(N)In chips, and convert it into green or blue-green visible-light. The CIE color coordinates of the as-fabricated LEDs are calculated and listed in Table 4. By varying Ba$^{2+}$ concentrations, the color of the as-fabricated LEDs can be tuned, but the adjustable zone is narrower than in the case of Ca$^{2+}$. It suggests that the color coordinates of pc-LEDs cannot be influenced by near UV Ga(In)N chips. However, the luminous efficiency decreases at first, and then increases with Ba$^{2+}$ content enhanced. The maximum luminous efficiency is 11.26 lm/W for 365 nm LEDs and 33.34 lm/W for 395 nm LEDs ($y = 0$). The variation of luminous efficiency of the as-fabricated LED is also consistent with the emission spectra due to the different phase formation.

![Intensity vs. Wavelength (nm) for 365 nm UV-Chips + Sr$_{0.90-y}$Ba$_y$Al$_2$O$_4$:Eu$^{2+}, \text{Dy}^{3+}$]

Figure 6. Cont.
Figure 6. Electroluminescence spectra of the as-fabricated LEDs based on UV-chip and Sr$_{0.90-x}$Ba$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors under 20 mA forward-bias current (i.e., $I_F = 20$ mA). Inset is chromaticity diagram of the as-fabricated LEDs: (a) 365 nm UV-chip; (b) 395 nm UV-chip; (c) Luminous efficiency of as-fabricated LEDs with different Ba$^{2+}$ content under $I_F = 20$ mA.

Table 4. Parameter of chromaticity coordinates based on Sr$_{0.90-x}$Ba$_x$Al$_2$O$_4$:0.05Eu$^{2+}$, 0.05Dy$^{3+}$ phosphors with 365 nm and 395 nm UV-Chips under 20 mA forward-bias current.

| $y$ Values | 395 UV-Chips | 365 UV-Chips |
|------------|--------------|--------------|
|            | CIE ($x$, $y$) | CIE ($x$, $y$) |
| $x$         | $y$          | $x$          | $y$          |
| 0.00        | 0.2782       | 0.2879       | 0.5471       | 0.5666       |
| 0.15        | 0.2369       | 0.2735       | 0.5045       | 0.5584       |
| 0.30        | 0.2412       | 0.2627       | 0.4612       | 0.5331       |
| 0.45        | 0.2127       | 0.2825       | 0.2568       | 0.4471       |
| 0.60        | 0.2071       | 0.2693       | 0.2881       | 0.4560       |
| 0.75        | 0.1864       | 0.2580       | 0.2309       | 0.4278       |
| 0.90        | 0.1839       | 0.2070       | 0.3678       | 0.4628       |
4. Conclusions

$\text{Sr}_{0.90-x}\text{Ca}_x\text{Al}_2\text{O}_4:0.05\text{Eu}^{2+}, 0.05\text{Dy}^{3+}$ and $\text{Sr}_{0.90-y}\text{Ba}_y\text{Al}_2\text{O}_4:0.05\text{Eu}^{2+}, 0.05\text{Dy}^{3+}$ ($x$ or $y = 0.00, 0.15, 0.30, 0.45, 0.60, 0.75, 0.90$) phosphors were synthesized. The variation of optical properties for the phosphors is ascribed to the phase structures. For the series of $\text{Sr}_{0.90-x}\text{Ca}_x\text{Al}_2\text{O}_4:0.05\text{Eu}^{2+}, 0.05\text{Dy}^{3+}$ phosphors, two heterogeneous structures coexist, except the samples with $x$(Ca$^{2+}$) = 0.00 and 0.90. The emission color of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{Dy}^{3+}$ phosphor can be adjusted largely from green to blue, and the lifetime can also be tuned largely from 1088.5 ms to 521.6 ms. For $\text{Sr}_{0.90-y}\text{Ba}_y\text{Al}_2\text{O}_4:0.05\text{Eu}^{2+}, 0.05\text{Dy}^{3+}$ phosphors, the phase transforms from monoclinic $\text{SrAl}_2\text{O}_4$ to hexagonal $\text{BaAl}_2\text{O}_4$ phase. Meanwhile, the emission wavelength shifts from 520 nm to 500 nm, and the color slightly changes from green to blue-green. More importantly, the average lifetime of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{Dy}^{3+}$ can be shortened from 842.04 ms to 219.91 ms, which can appropriately compensate for the AC time gap. Finally, the LEDs are successfully fabricated by combining the phosphors with Ga(In)N UV-chips. The maximum of luminous efficiency reaches 33.34 lm/W based on $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{Dy}^{3+}$ phosphors.

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