1 Introduction

Nowadays, white light-emitting diodes (LED) have attracted significant attention as next generation lighting devices due to their advantages of energy saving and long lifetime.1–6 To date, most commercial white LEDs have been fabricated via a combination of blue LED chips and yellow emitting Y3Al5O12:Ce3+ phosphors. However, these white LEDs exhibit a combination of blue LED chips and yellow emitting via most commercial white LEDs have been fabricated. Moreover, it shows lower color vividness because the cyan component in the range of 480–510 nm is weaker. Therefore, to adjust the emission band and enhance the emission band in the range of 480–510 nm, Ba2+ or Sr2+ ions with larger radii were introduced in NaCaPO4:Eu2+ with 0.03NaCl. The emission band showed an obvious blue shift. The colors varied from green (0.1996, 0.4380) to blue (0.1578, 0.0978) under the same excitation. Overall, the phosphor has promising applications for use in white LEDs.

2 Experimental

2.1 Sample preparation

A series of phosphors with the composition NaCaPO4:xEu2+ powder was synthesized, which can be used in a white LED.26 After this, green emission was enhanced in NaCaPO4:Eu2+. Tb3+ via energy transfer, according to Wang et al.27 In our study, to avoid a decreased luminescence efficiency due to energy transfer and save energy, the green emission of Eu2+ ions was enhanced by doping NaCl as an aid-sintering additive in NaCaPO4. Hence, a series of NaCaPO4-xEu2+:0.01Eu2+ phosphors was synthesized by a high temperature solid-state method. They showed a green emission band at 515 nm; however, the emission band ranging from 480 to 510 nm was weaker. Therefore, to adjust the emission band and enhance the emission band in the range of 480–510 nm, Ba2+ or Sr2+ ions with larger radii were introduced in NaCaPO4:Eu2+ with 0.03NaCl. The emission band showed an obvious blue shift, and the color ranged from green to blue with the increasing concentrations of Ba2+ or Sr2+ ions; thus, these phosphors can be used in white LEDs.
uniformly distributed. The obtained mixtures were heated at 1200 °C for 2 h in the reduction environment (95% H2 + 5% N2) and then naturally cooled down to room temperature to obtain the final phosphors.

2.2 Characterization

A Bruker D8 X-ray diffractometer was utilized to examine the X-ray powder diffraction (XRD) with Ni-filtered Cu Kα radiation (λ = 0.15418 nm), operating at 40 mA and 40 kV. The step length and diffraction range were 0.05° and 10–80°, respectively. To analyze the chemical composition of the phosphors, scanning electron microscopy (SEM) images and electron-dispersive X-ray (EDX) data were obtained by a Nova NanoSEM 650 with the accelerating voltage of 10 kV. Room temperature photoluminescence spectra of the samples were obtained via a Hitachi F-4600 fluorescence spectrophotometer using a 450 W Xe lamp as the excitation source, with the scanning wavelength ranging from 200 to 700 nm, scanning at 240 nm min⁻¹. The temperature-dependent luminescent properties were obtained using a computer-controlled electric furnace and a self-made heating attachment. Luminescence decay curves and quantum efficiencies of the samples were obtained using a Horiba FL-4600 fluorescence spectrophotometer. Herein, to obtain the luminescence decay curves, a nano-LED (370 nm) was used as the excitation source. The Commission International de l’Eclairage (CIE) coordinates for all samples were measured by a PMS-80 UV-VIS NEAR IR spectra analysis system.

3 Results and discussion

3.1 NaCaPO₄:0.01Eu²⁺ with tNaCl

NaCaPO₄:Eu²⁺ showed a broad emission band at 505 nm, according to our previous study. However, it showed weaker luminescence intensity. Hence, we introduced NaCl as an aid-sintering additive to enhance the emission intensity. To verify the influence of NaCl on the emission intensity, the concentration of Eu²⁺ was randomly fixed at 0.01 mol. Fig. 1 shows the XRD patterns of NaCaPO₄:0.01Eu²⁺ and NaCaPO₄:0.01Eu²⁺ with tNaCl (t = 0.01, 0.02, 0.03, 0.04, and 0.05). It can be seen that the XRD patterns of NaCaPO₄:0.01Eu²⁺ with tNaCl are indexed to NaCaPO₄ (JCPDS no. 29-1193) and no impurity phase was detected, indicating that NaCl has no influence on the phase of the phosphor. To further investigate the influence of NaCl on the phase of the phosphor, the crystal structure of NaCaPO₄:0.01Eu²⁺ with 0.03NaCl sample was refined using the General Structure Analysis System (GSAS) program. Fig. 2 shows the XRD pattern for Rietveld structure analysis of NaCaPO₄:0.01Eu²⁺ with 0.03NaCl based on the NaCaPO₄ phase model, and no impurity phase was detected. The final profile R-factors, Rwp, Rp, and χ² obtained were 8.62%, 6.19%, and 1.539, respectively, which suggested that the pure NaCaPO₄:0.01Eu²⁺ with 0.03NaCl was successfully synthesized. NaCaPO₄ was indexed to an orthorhombic crystal system and space group Pnam (a = 0.6797 nm, b = 0.9165 nm, c = 0.5406 nm, and V = 0.3368 nm³). The cell parameters and volume of NaCaPO₄:0.01Eu²⁺ with 0.03NaCl were a = 0.680 nm, b = 0.916 nm, c = 0.542 nm, and V = 0.3376 nm³, which are larger than those of NaCaPO₄, indicating that Eu²⁺ was doped into the host. The crystal structure of NaCaPO₄ viewed down the b-axis and the coordination polyhedron was composed of a Na/Ca/P atomic site, as shown in Fig. 2. A total of three independent Na and Ca cation polyhedral sites were available with the coordination number ranging from 6 to 8 in the unit cell of NaCaPO₄. Fig. 2 shows the presence of three different crystallographic Na environments: seven-coordinated Na(1) atom with
an average Na(1)–O distance of 0.260 nm, Na(2) atom surrounded by eight O atoms at the average distances of 0.264 nm, and a Na(3) atom that was nine-coordinated by nine O atoms at the average Na(3)–O distance of 0.268 nm. There were three crystallographic positions of Ca in the unit cell: seven-coordinated Ca2+ sites (Ca(1)) with the average Ca–O distance of 0.244 nm and two eight-coordinated Ca2+ sites (Ca(2)/Ca(3)) with the average Ca–O distance of 0.246 nm and 0.249 nm, respectively. P atoms with four-coordination modes could also be observed.

Fig. 3 shows the emission spectra of NaCaPO4:0.01Eu2+ and NaCaPO4:0.01-Eu2+ with tNaCl (t = 0.01, 0.02, 0.03, 0.04, and 0.05) excited at 365 nm. The inset shows the emission intensity at 515 nm depending on t concentration.

3.2 Na(Ba/Sr/Ca)PO4:Eu2+ with 0.03NaCl

3.2.1 Phase formation and structure. The XRD patterns and the magnified patterns between 22° and 24° of NaCaPO4:xEu2+ with 0.03NaCl with x = 0.001, 0.01, 0.03, and 0.05 are shown in Fig. 4a and b, respectively. It can be seen that all the peaks could be indexed to standard JCPDS no. 29-1193, suggesting that the phosphors are high-purity. According to the effective ionic radii of cations, Eu2+ ions were proposed to occupy the Ca2+ sites in NaCaPO4. The ionic radii for the seven- and eight-coordinated Ca2+ ions were 0.106 and 0.112 nm, respectively; thus, the Ca2+ sites in NaCaPO4 may be occupied by Eu2+ ions with similar ionic radii of 0.121 and 0.125 nm for the same coordination, respectively. The diffraction peaks of NaCaPO4:xEu2+ with 0.03NaCl slightly shifted to a lower angle, and it can be seen from Table 1 that the unit cell expanded with the increasing Eu2+ concentration. Because the radius of Ca2+ is

| Formula          | Cell parameters | Volumes |
|------------------|-----------------|---------|
|                  | a (nm)          | b (nm)  | c (nm)  | V (nm³) |
| NaCaPO4:0.01Eu2+ | 0.6798          | 0.9158  | 0.5412  | 0.3369  |
| NaCaPO4:0.01Eu2+ | 0.6800          | 0.9160  | 0.5420  | 0.3376  |
| NaCaPO4:0.03Eu2+ | 0.6810          | 0.9168  | 0.5430  | 0.3390  |
| NaCaPO4:0.05Eu2+ | 0.6815          | 0.9169  | 0.5464  | 0.3414  |

Fig. 5 XRD patterns of Na(BaSr/Ca)PO4:0.01Eu2+ with 0.03NaCl and standard data (JCPDS no. 33-1210).

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3.2.2 Luminescence properties

3.2.2.1 NaCaPO₄ₓEu²⁺ with 0.03NaCl. Fig. 8a–f show the emission spectra of NaCaPO₄ₓEu²⁺ with 0.03NaCl \((x = 0.001, 0.01, 0.03, 0.05, 0.07, \text{ and } 0.10)\) excited at 365 nm, respectively. We fitted the emission spectra with a Gaussian function for NaCaPO₄ₓEu²⁺ with 0.03NaCl. The orange dashed lines denote two Gaussian functions, which successfully fitted with the maxima at 510 (Eu²⁺) and 542 (Eu¹⁺) nm. Moreover, two different emission bands were obtained due to the different crystal surroundings of Eu²⁺ sites. From the XRD patterns and structural analysis, it can be inferred that Eu²⁺ ions occupied Ca²⁺ sites in NaCaPO₄. Hence, three distinct crystallographic sites were formed \(\text{(i.e., Ca(1), Ca(2), and Ca(3)), in which both the crystallographic sites of Ca(2) and Ca(3) were eight-coordinated).}\)

Therefore, the emission spectra were fitted by two Gaussian curves, and due to this, the luminescence of the luminescence centers with similar coordinate environments was indistinguishable, according to crystal field theory.²⁹ In addition, to investigate the relationship between the coordinate environment and emission peaks, the emission position of Eu²⁺ can be simply estimated using the Van Uitert eqn (1):²⁸,³¹

\[
E = Q \left[ 1 - \left( \frac{V}{4} \right)^{\frac{n}{2}} \times 10^{\frac{V}{25}} \right]
\]

where \(E\) is the energy location of the lower d-band edge for Eu²⁺ (\(\text{cm}^{-1}\)), \(Q\) is the energy location for the lower d-band edge of the free ion \((Q = 34 000 \text{ cm}^{-1} \text{ for Eu}^{2+})\), \(V\) is the valence of the active cation \((V = 2 \text{ for Eu}^{2+})\), \(n\) is the coordination number, and \(r\) is the radius of the host cation (Ca²⁺) replaced by the activator Eu²⁺ ion \((\text{Å})\). The value of \(E\) was difficult to obtain due to the complexity of the host, but it was constant in the same host. \(E\) is

3.2.2.2 NaSrPO₄ₓEu²⁺ with 0.03NaCl. All the diffraction peaks of the selected samples agreed well with the standard data for the NaCaPO₄ phase \(\text{(JCPDS no. 29-1193 and JCPDS no. 33-1282).}\)

XRD patterns of Na(Ba,Sr)PO₄:0.01Eu²⁺ with 0.03NaCl and NaBaPO₄ \((\text{JCPDS no. 33-1210)}\) are also shown as a reference in Fig. 5. We can see that Na(Ba,Sr)PO₄:0.01Eu²⁺ with 0.03NaCl can be basically indexed to the NaCaPO₄ phase \(\text{(JCPDS no. 29-1193)}\) when \(a \leq 0.5\). The phases of Na(Ba,Sr)PO₄:0.01Eu²⁺ with 0.03NaCl agreed well with the standard data for the NaBaPO₄ phase \(\text{(JCPDS no. 33-1210)}\) with the increase of \(a\).

To further investigate the phase formation depending on the Sr/Ca substitution of Na(Sr,Ca)PO₄:0.01Eu²⁺ with 0.03NaCl phosphors, XRD patterns for the selected samples were obtained and are shown in Fig. 6. All the diffraction peaks of the selected samples agreed well with the standard data for the NaCaPO₄ phase \(\text{(JCPDS no. 29-1193 and JCPDS no. 33-1282), indicating that Eu²⁺ ions were successfully incorporated in the host without noticeably changing the crystal structure.}\)

Fig. 7 SEM images and EDX spectra of NaCaPO₄:0.01Eu²⁺ with 0.03NaCl, Na(Ba,Sr)PO₄:0.01Eu²⁺ with 0.03NaCl \((a : b = 0.3 : 0.7)\) and Na(Sr,Ca)PO₄:0.01Eu²⁺ with 0.03NaCl \((c : d = 0.3 : 0.7)\).
542 nm (Eu1) emission bands correspond to Ca(2) (Ca(3)) and Ca(1), respectively.

Fig. 9a shows the emission intensities of 510 (Eu2) and 542 nm (Eu1) as a function of Eu$^{2+}$ contents; it can be observed that their emission intensities gradually increased before reaching the maximum at $x = 0.01$ for 510 nm emission and $x = 0.05$ for 542 nm emission, respectively. The emission intensities began to decrease with the increasing concentrations of Eu$^{2+}$ due to the concentration quenching effect, resulting from the non-radiative energy migration among the activator Eu$^{2+}$ ions.

Therefore, to further investigate the process of concentration quenching, the type of interaction among the activator Eu$^{2+}$ ions was calculated by the following equation:\(^{32-35}\)

$$I/x = K[1 + \beta(x)^{\theta}]^{-1}$$

(2)

where $I$ and $x$ represent the emission intensity and the concentration of the activator ion, respectively; $\beta$ and $K$ are the specific constants for a given host crystal and excitation condition, and $\theta = 3, 6, 8$ or 10 denotes the non-radiative energy transfer mechanism of exchange coupling, dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The fitted lines of log$(I/x)$ versus log($x$) for two emission bands centered at 510 and 542 nm are shown in Fig. 9b and c, respectively. The slopes of two fitted lines for 510 and 542 nm emission bands were $-1.14$ and $-0.99$, respectively. Therefore, the values of $\theta$ were $3.42$ and $2.97$, close to 3, implying that the main concentration quenching mechanism of Eu$^{2+}$ ions for both 510 and 542 nm emission bands in NaCaPO$_4$ host were the exchange coupling interactions. Fig. 9d shows the DR and excitation spectra of NaCaPO$_4$:0.01Eu$^{2+}$ with 0.03 NaCl, monitored at 510 and 542 nm. It can be seen that the DR spectrum matched well with the excitation spectra of NaCaPO$_4$:0.01Eu$^{2+}$ with 0.03NaCl. NaCaPO$_4$:0.01Eu$^{2+}$ with 0.03NaCl exhibited a broad absorption band from 200 to 450 nm, which was due to the transition of Eu$^{3+}$ that originated from 4f$^0$ ground state to 4f$^6$5d excitation state. For the excitation spectra monitored at 510 and 542 nm, the spectral width at 542 nm was larger than that at 510 nm due to emission bands that originate from different Eu$^{2+}$ luminescence centers.

To further study the reason for different excitation spectra monitored at 510 and 542 nm, their decay curves were measured, as shown in Fig. 10a and b, respectively. A single exponential was used to fit the decay curves, and the effective lifetimes could be defined as:\(^{36,37}\)

$$\tau = \int_0^\infty \frac{I(t)dt}{\int_0^\infty I(t)dt}$$

(3)

where $I(t)$ is the emission intensity at time $t$ and $\tau$ is the decay lifetime. The corresponding lifetimes at 510 and 542 nm for NaCaPO$_4$:xEu$^{2+}$ with 0.03NaCl are shown in Fig. 10a and b, respectively. For example, the lifetimes of NaCaPO$_4$:0.01Eu$^{2+}$ with 0.03NaCl for 510 and 542 nm emission bands were calculated to be 339.01 ns and 320.22 ns, respectively, which implies that two emission bands were attributed to two different Eu$^{2+}$ ion luminescence centers.

proportional to the $n$ and $r$ of the sample; hence, Eu$^{2+}$ ions with a higher coordination number generally emit at a higher energy, corresponding to a lower wavelength. As a result, 510 (Eu2) and 542 nm (Eu1) emission bands correspond to Ca(2) (Ca(3)) and Ca(1), respectively.
3.2.2.2 Na(Ba\textsubscript{a}Ca\textsubscript{b})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl and Na(Sr\textsubscript{c}Ca\textsubscript{d})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl.

Samples were synthesized using a fixed Eu\textsuperscript{2+} concentration of 0.01. The normalized emission spectra of Na(Ba\textsubscript{a}Ca\textsubscript{b})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl and Na(Sr\textsubscript{c}Ca\textsubscript{d})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl are shown in Fig. 11a and b, respectively, excited at 365 nm. It can be seen that the emission spectra of Na(Ba\textsubscript{a}Ca\textsubscript{b})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl show an obvious blue shift with an increase in Ba\textsuperscript{2+} ions. However, when the ratio of Ba and Ca exceeded 0.5 : 0.5, the full width at half maximum decreased. For Na(Sr\textsubscript{c}Ca\textsubscript{d})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl, the emission spectra show a broadened full width at half maximum with the increasing Ba\textsuperscript{2+} ions. Based on the abovementioned discussion, the emission spectra could be deconvoluted into two Gaussian components with the maxima at 510 nm (Eu(2)) and 542 nm (Eu(1)).

For Na(Ba\textsubscript{a}Ca\textsubscript{b})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl and Na(Sr\textsubscript{c}Ca\textsubscript{d})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl, the fitted spectra of 510 nm and 542 nm are shown in Fig. 12a–d. The intensities of the 510 nm and 542 nm spectra for Na(Ba\textsubscript{a}Ca\textsubscript{b})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl increased with the increasing Ba\textsuperscript{2+} concentration up to a : b = 0.2 : 0.8. Due to the concentration quenching effect, the intensities decreased with further increase in the concentration of Ba\textsuperscript{2+} ions. For Na(Sr\textsubscript{c}Ca\textsubscript{d})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl, the intensities of 510 nm and 542 nm are shown in Fig. 12c and d. The intensities of 510 nm and 542 nm for Na(Ba\textsubscript{a}Ca\textsubscript{b})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} and Na(Sr\textsubscript{c}Ca\textsubscript{d})PO\textsubscript{4}:0.01Eu\textsuperscript{2+} with 0.03NaCl excited at 365 nm.
542 nm increased and reached maxima at $c : d = 0.3 : 0.7$ and then decreased with the increment of Sr$^{2+}$ ions concentration. Fig. 13a–d show the normalized spectra of 510 nm and 542 nm for Na(Ba$_a$Ca$_b$)PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl and Na(Sr$_c$Ca$_d$)PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl excited at 365 nm. For Na(Ba$_a$Ca$_b$)PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl, it can be seen that the spectra of 510 nm and 542 nm shifted to a lower wavelength, as shown in Fig. 13a and b, respectively. Moreover, the full width at half maximum of the 510 nm spectra for Na(Ba$_a$Ca$_b$)PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl decreased when the ratio of Ba to Ca exceeded 0.5 : 0.5. However, for Na(Sr$_c$Ca$_d$)PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl, the full width at half maximum of 510 nm spectra decreased when the radio of Sr and Ca was greater than 0.7 : 0.3, and no shift could be observed. The 542 nm spectra showed a blue shift with the increase of Sr$^{2+}$ ions. Generally, the crystal field splitting ($D_q$) trends with bond length can be determined by the following equation:

$$D_q = \frac{Ze^2r^4}{6R^5}$$

where $D_q$ is the magnitude of the 5d energy level separation, $Z$ represents the anion charge or valence, $e$ is the electron charge, $r$ is the radius of the d wave function, and $R$ is the bond length. The bond length of Ce–O will increase due to the lattice expansion because the radii of Ba$^{2+}$ and Sr$^{2+}$ are larger than that of Ca$^{2+}$. Hence, the crystal field splitting will become weaker, which causes a blue shift and decreases full width at half maximum. The schematic mechanism of the decreased full width at half maximum and blue shift of Eu$^{2+}$ emission is shown in Fig. 14 when Ba$^{2+}$ and Sr$^{2+}$ were substituted for Ca$^{2+}$ in NaCaPO$_4$:0.01Eu$^{2+}$ with 0.03NaCl. The blue shift of Na(Ba$_a$Ca$_b$)PO$_4$:0.01Eu$^{2+}$ with 0.03 NaCl was greater than that of Na(Sr$_c$Ca$_d$)PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl, which is due to that fact that the radius of Ba$^{2+}$ ($r_{Ba} = 1.34$ nm) is larger than that of Sr$^{2+}$ ($r_{Sr} = 1.12$ nm). The crystal field splitting of Na(Ba$_a$Ca$_b$)PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl was weaker, and a more obvious blue shift could be observed. For Na(Sr$_c$Ca$_d$)PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl, comparing the decreased full width at half maximum of the 510 nm band and the blue shift of the 542 nm band, the difference may be that Eu$^{2+}$ had different coordinations (i.e., eight and seven coordination). Therefore, the emission properties could be tuned by controlling the concentration of Ba$^{2+}$ or Sr$^{2+}$. Fig. 15a and b show CIE chromaticity coordinates and images of Na(Ba$_a$Ca$_b$)PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl and
Na(Sr\(_{c}\)Ca\(_{d}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl under a 365 nm UV lamp. It can be seen that the emission color of Na(Ba\(_{a}\)Ca\(_{b}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl and Na(Sr\(_{c}\)Ca\(_{d}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl could change from green (0.1996, 0.4380) to blue (0.1578, 0.0978) or to cyan (0.2285, 0.2853), respectively. The corresponding images of the samples are shown in Fig. 15.

For LED applications, the thermal stability of the phosphor is one of the important parameters. The temperature-dependent emission spectra of Na(Ba\(_{0.7}\)Ca\(_{0.3}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl and Na(Sr\(_{0.8}\)Ca\(_{0.2}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl under the excitation of 365 nm were investigated, as shown in Fig. 16a and b, respectively. It was observed that the emission intensity continuously decreased with the increasing temperature from room temperature to 200 °C. The emission intensity of Na(Ba\(_{0.7}\)Ca\(_{0.3}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl and Na(Sr\(_{0.8}\)Ca\(_{0.2}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl decreased to 90% and 76% of the initial emission intensity, respectively, corresponding to 100 °C. It can be seen that the thermal quenching of Na(Sr\(_{0.8}\)Ca\(_{0.2}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl was inferior to that of Na(Ba\(_{0.7}\)Ca\(_{0.3}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl. The reason is that in Na(Ba/Sr/Ca)PO\(_4\):Eu\(^{2+}\) with NaCl, with the replacement of Eu\(^{2+}\)–Eu\(^{2+}\) neighbors by Eu\(^{2+}\)–Ba\(^{2+}\)/Sr\(^{2+}\) pairs, the emission intensity will decrease with an increment in temperature due to the lower nonradiative decay rate from the lowest excited state, according to Peng et al.\(^{41}\) The bond length will become shorter when Ba\(^{2+}\) is co-doped in NaCaPO\(_4\):Eu\(^{2+}\) with NaCl with respect to Sr\(^{2+}\) co-doping because the radius of Ba\(^{2+}\) is larger than that of Sr\(^{2+}\). The thermal excitation from Eu\(^{2+}\)–Ba\(^{2+}\)/Sr\(^{2+}\) may occur differently with an increase in temperature. Hence, co-doping Sr will lead to worse thermal quenching compared to co-doping Ba due to covalent effects. The slightly decreased intensity indicated that the Na(Ba/Sr/Ca)PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl phosphor could be applied to a white LED. To investigate the relationship of luminescence with temperature and to calculate the activation energy from thermal quenching, the activation energy (\(E_a\)) can be expressed by the following formula:\(^{42}\)

\[
I = I_0/[1 + c \exp(-E_a/kT)]
\]

where \(I\) and \(I_0\) are the luminescence intensities of the phosphor at the testing temperature and room temperature, respectively, \(E_a\) represents the thermal quenching activation energy of the phosphor, \(c\) is the rate constant for thermally activated escape, and \(k\) is the Boltzmann constant (8.629 × 10\(^{-5}\) eV K\(^{-1}\)). The inset of Fig. 16a and b show the plots of ln[\((I_0/I) - 1\)] versus 1/T for Na(Ba\(_{0.7}\)Ca\(_{0.3}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl and Na(Sr\(_{0.8}\)Ca\(_{0.2}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl, respectively. The calculated \(E_a\) were 0.1506 and 0.2399 eV for Na(Ba\(_{0.7}\)Ca\(_{0.3}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl and Na(Sr\(_{0.8}\)Ca\(_{0.2}\))PO\(_4\):0.01Eu\(^{2+}\) with 0.03NaCl, which indicate that the phosphors show relatively good thermal stability and can be used in an LED.

To verify the actual application of the phosphor, we chose the sample with the broadest full width at half maximum to fabricate...
Fig. 17 (a) Diagram of white LED package. (b) CIE chromaticity coordinates and photos of white LED, which is fabricated by Na[Ba$_{0.7}$Ca$_{0.3}$]PO$_4$:0.01Eu$^{2+}$ with 0.03 NaCl and (CaSr)AlSiN$_3$:Eu$^{2+}$ phosphors. (c) Electroluminescence spectra of white LED composed of a 380 nm UV chip.

A white LED. The devices were combined with a 380 nm UV chip (CaSr)AlSiN$_3$:Eu$^{2+}$ and Na[Ba$_{0.7}$Ca$_{0.3}$]PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl phosphors, Fig. 17a. CIE coordinates were (0.3750, 0.3634), and the image shows an excellent white light, as shown in Fig. 17b. Fig. 17c shows the electroluminescence spectrum of the white LED. It can be seen that the spectrum shows a stronger emission in the range of 480–510 nm. The quantum efficiency of Na[Ba$_{0.7}$Ca$_{0.3}$]PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl was 45.06%. Therefore, Na[Ba/Sr/Ca]PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl has potential applications in white LEDs.

4 Conclusions

In summary, a series of Na[Ba/Sr/Ca]PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl phosphors were synthesized via a high-temperature solid-state reaction method. On the one hand, the luminescence intensity of NaCaPO$_4$:Eu$^{2+}$ was enhanced using NaCl as the aid-sintering additives, and the phases were indexed to pure NaCaPO$_4$. NaCaPO$_4$:Eu$^{2+}$ exhibited the strongest emission when the concentration of NaCl was 0.03. NaCaPO$_4$:Eu$^{2+}$ with 0.03NaCl exhibited two green emission bands at 510 and 542 nm, which were ascribed to two different Ca sites with different coordination (i.e., eight and seven coordination). On the other hand, by gradually introducing Ba$^{2+}$ or Sr$^{2+}$ into NaCaPO$_4$:0.01Eu$^{2+}$ with 0.03NaCl, 510 and 542 nm emission bands showed various full width at half maximum and a blue shift caused by the crystal field splitting. The intensity of cyan region from 480 to 510 nm increased by controlling the Ba or Sr concentration. Compared to a Sr$^{2+}$-doped phosphor, Na[BaCa]PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl exhibited a more obvious blue shift because the radius of Ba$^{2+}$ is larger than that of Sr$^{2+}$. Therefore, luminescence of Na[Ba/Sr/Ca]PO$_4$:0.01Eu$^{2+}$ with 0.03NaCl could be tuned from green (0.1996, 0.4380) to blue (0.1578, 0.0978) under the same excitation by introducing Sr$^{2+}$ or Ba$^{2+}$ ions. Moreover, these phosphors can be used in UV/n-UV-pumped white LEDs.

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