Review—Narrow-Band Nitride Phosphors for Wide Color-Gamut White LED Backlighting

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To achieve a brilliant image with high color saturation in white LED backlighting technology, innovative phosphor materials with narrow-band emission in the green and red spectral region are continuously pursued. Nitride phosphors are so far accepted as the most suitable phosphors for white LED backlights due to their high efficiency and excellent robustness. In this perspective, we will present an overview about the recent developments of state-of-the-art and newly-emerging nitride phosphors with a narrow emission band, and the emphasis would be placed on the relationships between the crystal structure and luminescence properties. Finally, some empirical rules for designing novel narrow-band phosphors for backlighting technologies would be summarized.

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Nowadays, liquid crystal displays (LCDs) are ubiquitous in our daily lives, and their applications range from smartphones, tablets, computers, to large-screen TVs, and data projectors. As there is much concern on backlight units with larger color gamut, higher brightness, lower power consumption and mercury-free, white light-emitting diodes (LEDs) have been widely applied as backlighting components in modern LCD technologies to replace the traditional cold cathode-fluorescence lamps (CCFLs).1-12

Multi-chip white LEDs, which comprise red-, green- and blue-emitting chips, exhibit excellent color performance and tuning abilities. However, the efficiencies of red, green, and blue LEDs vary over time at different rates. In addition, separated driving circuits and complicated feedback-driven systems are required, which leads to a high cost. Moreover, the efficiency of green LEDs, known as “green gap”, is much smaller than that of red and blue ones.13-15 By contrast, phosphor-converted (pc) white LED backlights, which combine a single LED chip with phosphor materials, are mostly used due to their high efficiency, cost effectiveness and robustness. To achieve a large color gamut and to faithfully reproduce the natural colors, the emission peak of phosphors should match well with the RGB color filters of LCDs. Phosphors with narrow emission bands would loss less their luminescence after passing through color filters, and also promise high color purity. Therefore, narrow-band phosphors with appropriate emission maximum are required for high efficiency and wide color gamut backlights.13,15

Quantum dots (QDs) materials have shown great potentials for next-generation displays due to their narrow emission band.13-12 In comparison to traditional CCFL having a color gamut of ~75% of the National Television Standard Committee (NTSC) standard, the Cd-containing QDs-integrated white LED backlights promise a large color gamut of > 100% NTSC, but the application has been limited due to the usage restrictions of hazardous Cd compounds. Compared to Cd-containing rivals, the non-toxic InP/ZnS QDs only yield a color gamut of 87% NTSC due to the quite broader emission band.11 Moreover, it is difficult to maintain the initial optical properties of the QDs during device fabrication and long-term operation.

On the other hand, a blue LED covered with a combination of rare-earth-doped green and red narrow-band phosphors have been proposed to systematically achieve improvements in color gamut.14-16 Ito et al. attempted the application of narrow-band SrGa2S4:Eu2+ (green) and CaS:Eu2+ (red) phosphor sheets in white LED backlights, and obtained a large color gamut of 90% NTSC, but limitations such as strong thermal quenching and high sensitivity toward moisture hindered the practical application of sulfide phosphors to some extent.4 Over the past decade, rare-earth-doped nitride or oxynitride phosphors have been vindicated to be excellent down-conversion luminescent materials in white LEDs due to their superiorities over others. The narrow-band nitride phosphors are also accepted as the most suitable phosphors for white LED backlights due to their high efficiency and excellent robustness. For example, Xie et al. has developed a wide color gamut of 92% NTSC by pumping β-Sialon:Eu2+ (green) and CaAlSiN3:Eu2+ (red) nitride phosphor with a blue LED chip.2 Fukuda et al. has succeeded in using Sr3Si2Al2O9:N2:Eu2+ (green) and CaAlSiN3:Eu2+ (red) phosphors to fabricate a white LED backlight with a color gamut of 94.2%.6 Yoshimura et al. has achieved a superwide color gamut of >100% by using narrow-band γ-ALON:Mn2+,Mg2+ (green) and K2SiF6:Mn2+ (red) phosphors.16

To meet the requirements of backlighting technologies, new types of narrow-band nitride phosphors with enhanced or specialized properties are continuously pursued by chemists or materials scientists. Recently, Pust et al. reported the discovery of a highly promising narrow-band red phosphor, SrLiAl11N12:Eu2+, with an emission peak position at 650 nm and a full width at half-maximum (FWHM) of 50 nm,7 while the chemically similar CaLiAl11N12:Eu2+ narrow-band red-emitting phosphor has a deep-red emission peak at 668 nm with the FWHM of 60 nm.18 Another narrow-band red phosphor, SrMg2SiN4:Eu2+, has an ideal peak position at 615 nm and a narrow bandwidth of only 43 nm.16 Takeda et al. have discovered a narrow-band green phosphor Ba2Li2Si2AlN3:Eu2+ peaking at approximately 515 nm with FWHM of 61 nm via the single particle diagnosis approach.20 Strobel et al. have reported a narrow-band green phosphor Ba2Li2(Al2Si2)N6:Eu2+ peaking at 532 nm with FWHM of 57 nm by using the single crystal X-ray diffraction method.21

Therefore, the focus in this regard is on some commonly used and newly-emerging narrow-band nitride phosphors and to highlight the important structural principles to realize the narrow emission bands. Firstly, state-of-the-art and newly-discovered narrow-band green and red nitride phosphors with narrow emission bands have been demonstrated. Then, the emphasis would be placed on the relationships between the crystal structure and luminescence properties. Finally, some empirical rules for designing novel narrow-band phosphors for white LED backlighting technologies would be presented.

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Figure 1. (a) Crystal structure of \( \beta \)-SiAlON, in which there are two distinct nitrogen sites with Wyckoff symbols 2c and 6b. (b) The calculated potential energy surface of (001) plane for \( \beta \)-SiAlON using density functional theory, and the low energy regions shown in violet indicate the most favorable interstitial position for the incorporation of Eu\( ^{2+} \). (Reproduced with permission from Refs. 23 and 24, copyright 2014, 2016, American Chemical Society, American Institute of Physics).

**Narrow-Band Green Phosphors**

\( \beta \)-SiAlON:Eu\( ^{2+} \)—\( \beta \)-SiAlON is derived from \( \beta \)-Si\( _3 \)N\( _4 \) (hexagonal system, space group P6\( 3 / m \)) by partial substitution of Si by Al and N by O, and its chemical formula can be written as Si\(_{6-\beta}\)Al\(_{\beta}\)N\(_6\)\(_{1-\beta}\), with \( \beta \) typically ranging from 0 to 4.2. The crystal structure shown in Fig. 1a tells that the densely packed, corner-sharing (Si,Al)\( (N,O)_4 \) tetrahedra form a three-dimensional network with a one-dimensional channel running along the c-axis.\(^{22,23}\) Density functional theory (DFT) calculations based on the Vienna ab initio Simulation Package (VASP) are used to generate the potential energy surface, as illustrated in Fig. 1b.\(^{24}\) Visualization of the (001) plane reveals the favorable interstitial site for Eu\( ^{2+} \), that is, Eu\( ^{2+} \) is likely to sit at the interstitial (violet region) in the large hexagonal channels along the [0001] direction.

Up to now, many researches have focused on revealing the atomic site of Eu\( ^{2+} \) in the \( \beta \)-SiAlON lattice. Li\(^{25}\) et al. first theoretically predicted that Eu\( ^{2+} \) ion was interstitially situated within the channels parallel to the c-axis and directly connected by six adjacent nitrogen atoms ranging 2.4850–2.5089 Å. Then Kimoto\(^{26}\) et al. directly observed the interstitial Eu\( ^{2+} \) in the large hexagonal channels coordinated by Si\(_{6-\beta}\)Al\(_{\beta}\)N\(_6\)\(_{1-\beta}\) tetrahedra utilizing scanning transmission electron microscopy (STEM) technique, as shown in Figs. 2a–2b. The annular dark-field STEM image clearly shows the Eu dopant at the origin, as indicated by an arrow. In other words, a single Eu\( ^{2+} \) ion is observed in the atomic channel of the \( \beta \)-SiAlON matrix. Later, Brgoch\(^{27}\) et al. proposed that the Eu\( ^{2+} \) ion occupied a distorted 12-coordinate interstitial site in the hexagonal channels via extended X-ray absorption fine structure (EXAFS) measurements. Recently, Wang\(^{23}\) et al. suggested a highly unusual Eu\( _{0.125} \)N\(_{0.875}\) coordination polyhedron using first-principles calculations, and this special coordination environments were highly responsible for the electronic structure characteristic, i.e., a large splitting of > 0.1 eV between the two highest Eu\( ^{2+} \)d bands, which ensures the unique narrow-band emission. The Eu\( ^{2+} \) local environments for two representative compositions, \( \beta \) = 0.125 and 0.208, were calculated by Wang\(^{23}\) as shown in Figs. 2c–2d. The Eu-N bonds can be classified into two types, three shorter Eu-N bonds of 2.488–2.516 Å and six longer Eu-N bonds of 2.745–2.826 Å, which are in a good agreement with the estimated values from previous EXAFS fitting by Brgoch.\(^{24}\)

\( \beta \)-SiAlON can be readily prepared by a variety of methods, such as solid-state reaction,\(^{28}\) gas pressure sintering,\(^{29}\) and combustion synthesis.\(^{30}\) Hirotsui\(^{28}\) et al. firstly reported Eu\( ^{2+} \)-activated \( \beta \)-SiAlON phosphors with the composition of Eu\(_{0.0296}\)Si\(_{5.2085}\)Al\(_{0.1353}\)O\(_{10.0084}\)N\(_{6.5628}\) (\( \beta \) = 0.17), which yields an ideal emission peak of 535 nm and a narrow bandwidth of 55 nm. Later, systematical investigations have been conducted to clarify the influences of \( \beta \) value and Eu\( ^{2+} \) concentration on phase purity and photoluminescence properties.\(^{31,32}\) Fig. 3a shows the XRD patterns of \( \beta \)-SiAlON with varying \( \beta \) values. Single \( \beta \)-SiAlON phase can be obtained in samples with \( \beta \) = 0.1 and 0.5. Higher \( \beta \) values of 1.0, 1.5, and 2.0 lead to impurity phase formation, and the amount of secondary phases increases with \( \beta \) value. Fig. 3b shows the photoluminescence spectra for samples with small \( \beta \) (\(<0.25\) values, which exhibit fine structure with several sharp peaks.\(^{33}\) The excitation band covers a broad range of 250–500 nm, allowing excitation by a variety of commercial LED chips. The intense narrow-band emission of Eu\( ^{2+} \) corresponds to the allowed 4\( f^6\)5\( d \)-4\( f^7 \) transition of Eu\( ^{2+} \). As \( \beta \) value decreases, the emission maximum shifts to short wavelengths (i.e., blueshift). Meanwhile, the emission bandwidth decreases from 55 to 45 nm. Fig. 3c depicts the peak emission wavelength as a function of \( \beta \) value and Eu\( ^{2+} \) concentration. It is found that the emission peak can be tuned in a wide range of 528–550 nm via composition tailoring.

With increasing \( \beta \) value and Eu\( ^{2+} \) concentration, the emission band shifts toward the long wavelength side (i.e., redshift), and higher \( \beta \) values (>1) cause red-shifted emission (\( \lambda_{\text{em}} = 545–550 \) nm) along with broadened bandwidth (>63 nm). Therefore, limits on \( \beta \) < 0.5 is established for practical applications. Moreover, the oxygen content is proven to have a great impact on the photoluminescence properties. Takahashi\(^{34}\) et al. synthesized \( \beta \)-SiAlON:Eu\( ^{2+} \) phosphors with low oxygen concentrations in the range of 0.3–0.7 wt.%. The variation of emission bandwidth is very distinct, decreasing from 53 to 47 nm with reduced oxygen concentration.

\( \beta \)-SiAlON:Eu\( ^{2+} \) also shows excellent thermal quenching resistance. For example, the emission intensity of the sample \( \beta \) = 1.0 at 150 °C maintains 84–87% of that measured at room temperature, as shown in Fig. 3d. The thermal quenching of samples becomes smaller with \( \beta \) ranging from 0.1 to 1.5, and the sample of \( \beta \) = 1.5 exhibits the best thermal property. Recently, Wang\(^{23}\) et al. have reported that the predicted barrier of thermal ionization for \( \beta \)-SiAlON:Eu\( ^{2+} \) is relatively high (~0.56–0.68 eV), which is in good accordance with its experimentally measured excellent thermal stability.

More recently, first-principles calculations have been utilized to understand the structure-composition-property relationships in \( \beta \)-SiAlON:Eu\( ^{2+} \). Wang\(^{25}\) et al. demonstrated that \( \beta \) value (Si/Al ratio or oxygen concentrations) could have a significant effect on the local environment of Eu\( ^{2+} \) in \( \beta \)-SiAlON. As shown in Fig. 4, increasing \( \beta \) leads to an elongation in the Eu-N bond length and the enhanced distortion of Eu\( _{0.1} \) polyhedron. The magnitude of the crystal field...
splitting is related to the activator-anion local geometry, which can be described by the average bond length ($l_{av}$) and distortion index ($D$) of the activator-anion polyhedral. Shorter $l_{av}$ and higher $D$ typically lead to a larger splitting. Both $l_{av}$ and $D$ increase with increasing $z$ at constant Eu$^{2+}$ concentration ($y$ value). However, the percentage increase in $D$ is 3.32%, 5 times larger than the increase in $l_{av}$ (0.63%). Therefore, the effect of increasing $D$ dominates over the increase in $l_{av}$, resulting in a larger crystal field splitting with increasing $z$, thereby causing a red-shifted emission.

Fig. 5a shows a schematic of the different transitions in broad- and narrow-band phosphors. In both cases, the main emission is the result of the transition of an electron from the lowest $5d$ band into the empty $4f$ top band, i.e., a $4f^{6}5d^{1}$ → $4f^{7}$ transition. When there are multiple Eu$^{2+}$ $4f$ levels within 0.1 eV from the highest band, overlapping emissions result in a broad bandwidth. Conversely, a large energy splitting, $\Delta E_S > 0.1$ eV between the two highest $4f$ bands results in a narrow-band emission. Therefore, $\Delta E_S > 0.1$ eV was proposed as a threshold for narrow-band emission. The $E_S$ values were calculated with $z$ ranging from 0.125 to 0.75, as shown in Fig. 5b. We may observe that $\Delta E_S$ at low $z$ values are greater than 0.1 eV, implying a narrow emission band. On the other hand, $\Delta E_S$ at a large $z = 0.75$ is less than 0.1 eV, indicating broadening in emission spectra. The calculated results suggest that the synthesis should be directed toward achieving lower $z$ value or oxygen content in β-SiAlON in order to achieve narrower emission bands and to minimize the red-shift, which are in line with previous experimental observations.

In order to understand the distribution of Al and O in β-SiAlON structure, Cozzan et al. utilized high-resolution NMR techniques in combination with DFT calculations to unravel the exquisite details of local compositional variation in the crystal structure. As shown in Fig. 6, Al NMR spectral features are assigned to different AlO$_N$ species ($0 \leq N \leq 4$) species, and these results suggest unambiguously a definite preference for AlO$_4$ formation and a decrease in the AlN$_4$ and AlO$_2$N$_2$/AlO$_3$N$_2$ populations. This is in stark contrast to the stochastic nature of Al and O distribution in the crystal structure.
Figure 5. (a) Relationship between emission bandwidth and Eu$^{2+}$ 4f band levels. (b) Plot of calculated bandwidth descriptor $\Delta E_s$ as a function of $z$. Red circles and green stars indicate compositions with the same $z/y$ ratio and same $y$ (y defining the Eu$^{2+}$ activator concentration and z tuning the Si/Al ratio, or equivalently, the oxygen concentration). (Reproduced with permission from Ref. 27 and 23, copyright 2016, American Chemical Society).

distribution of Al and O on the $\beta$-Si$_3$N$_4$ framework, which predicts a high population of AlN$_4$ environments, a low population of AlON$_3$ tetrahedra, and virtually no AlO$_2$N$_2$/AlO$_3$N (see Fig. 6d). In other words, despite the high dilution of both Al and O in the framework, Al and O have a surprising clustering in the $\beta$-SiAlON structure, which in turn leads to lower host structural rigidity.24

$\gamma$-AlON:Mn$^{2+}$.—$\gamma$-AlON is a solid-solution compound in the AlN-Al$_2$O$_3$ binary system with AlN concentration of 27–40 mol%.38 It shows a face-centered cubic and nonstoichiometric spinel structure (space group $Fd\bar{3}m$). In the three-dimensional rigid network, Al atoms occupy both tetrahedral (8a) and octahedral (16d) sites which are coordinated by four and six anions, respectively, and the O/N atoms occupy the anion sites of a spinel lattice (32e), as depicted in Fig. 7. In addition, $\gamma$-AlON contains vacancies as regular part of the crystal, which are mainly distributed in the octahedral site.39,40

When doped with Mn$^{2+}$ or rare earths, $\gamma$-AlON can be developed into interesting luminescent materials. Xie et al. reported that this phosphor produced an interesting green emission band at 512 nm and a FWHM of 32 nm upon 445 nm excitation, which shows a shorter and narrower emission spectrum than $\beta$-SiAlON:Eu$^{2+}$. This indicates that $\gamma$-AlON:Mn$^{2+}$ could promise a higher color purity than $\beta$-SiAlON:Eu$^{2+}$. However, $\gamma$-AlON:Mn$^{2+}$ has a quite low absorption efficiency (only 21% under 450 nm excitation) due to the spin-forbidden transition of 3$d^5$ electrons in Mn$^{2+}$. Later, it is found that the green luminescence band of $\gamma$-AlON:Mn$^{2+}$ can be significantly enhanced by the addition of Mg$^{2+}$ ion into $\gamma$-AlON:Mn$^{2+}$. The photoluminescence properties of Mn$^{2+}$-, and Mn$^{2+}$-Mg$^{2+}$ codoped $\gamma$-AlON are shown in Fig. 8. The excitation spectra of both samples consist of five peaks at 340, 358, 381, 424, and 445 nm, and the emission spectra show a single band centered at 512 and 520 nm for Mn$^{2+}$- and Mn$^{2+}$-Mg$^{2+}$ doped samples, which correspond to the characteristic transition of Mn$^{2+}$ 4T$_1$ (4G) $\rightarrow$ 6A$_1$. 

Figure 6. $^{27}$Al NMR spectra at 18.8 T and 20 kHz MAS for $z =$ (a) 0.050, (b) 0.075, and (c) 0.125 demonstrating the increase in the contribution from AlON$_3$ as a function of increasing Al. (d) Populations obtained from fitting the experimental NMR data (closed shapes) and stochastic model (open shapes). (Reproduced with permission from Ref. 37, copyright 2017, American Chemical Society).
Figure 7. Crystal structure of spinel γ-AlON, showing the AlO_4 tetrahedra and AlO_6 octahedra. Red: 32e anion, orange: 8a cation, blue: 16d cation or vacancy.

The Mn^{2+}-Mg^{2+} co-doped sample yields 1.7 times of the emission intensity of the sample containing only Mn^{2+}, and the emission band is red-shifted with the FWHM increasing from 32 to 44 nm (see Fig. 8a). Xie et al. proposed that the luminescence improvement by Mg^{2+} addition was attributable to the significant reduction of the impurity corundum phase. Kitaura et al. have chased the effect of Mg^{2+} co-doping on ESR spectra of γ-AlON:Mn^{2+}, and it turns out that the Mg^{2+} co-doping increases the quantity of Mn^{2+} ions at the tetrahedral Al^{3+} sites and finally leads to the luminescence enhancement. Fig. 8b presents the temperature dependent luminescence intensity of γ-AlON:Mn^{2+}-Mg^{2+}. The emission intensity measured at 150°C maintains 88% of that at room temperature, which is comparable to that of SiAlON-based phosphors. Fig. 8c tells that γ-AlON:Mn^{2+}-Mg^{2+} has a sharper emission spectrum on the long-wavelength side than the β-SiAlON:Eu^{2+} phosphor. Thanks to the narrower and blue-shifted emission spectrum, white LED backlighting devices using γ-AlON:Mn^{2+}-Mg^{2+} as green phosphor achieve a color gamut larger than 100% of the NTSC, whereas the color gamut is only 95.7% relative to NTSC using β-SiAlON:Eu^{2+} as green phosphor (see Fig. 8d). X-ray absorption fine structure (XAFS) analyses are commonly used to reveal the electronic state and coordination structure of specific elements. Takeda et al. studied the valence and coordination structure of Mn in the γ-AlON:Mn-Mg green phosphor by XAFS technique, as shown in Fig. 9. The absorption edge of Mn K-edge XANES spectrum for Mn,Mg-codoped γ-AlON is located at 6542.5 eV, in between those of MnO and MnCO_3. From comparisons with the XANES spectra of various manganese oxides, the valence of the Mn ions is proven to be divalent. Further, the EXAFS analyses of Mn K-edge reveal that Mn^{2+} ions are predominantly placed at tetrahedral Al sites (see Fig. 9b). To determine the Mg sites in AlON structure, total energy with different Mg occupation sites is calculated to confirm that Mg occupation at tetrahedral sites is more favorable. That is to say, although Al atoms occupy both tetrahedral and octahedral sites, Mn and Mg substitute the Al atoms only in the tetrahedral sites. This is also in line with the luminescent properties because the emission of Mn^{2+} strictly depends on the crystallographic site where it occupies, and Mn^{2+} emits green light when it resides in a tetrahedron and red light in an octahedron.

Figure 8. (a) Excitation and emission spectra of Mn^{2+}, and Mn^{2+}-Mg^{2+} codoped γ-AlON; (b) Temperature dependent luminescence of Mn^{2+}-Mg^{2+} codoped γ-AlON; (c) Emission spectra of Mn^{2+}-Mg^{2+} codoped γ-AlON and β-SiAlON:Eu^{2+}; (d) Color gamut of the white LED displays fabricated using γ-AlON:Mn^{2+}-Mg^{2+} or β-SiAlON:Eu^{2+} as green phosphor. (Reproduced with permission from Refs. 41 and 16, copyright 2008, 2017, American Institute of Physics, Institute of Pure and Applied Physics).
Another strategy to improve the low absorption of Mn$^{2+}$ is to co-dope a sensitizer that transfers its energy to Mn$^{2+}$. Eu$^{2+}$ is reported to be an efficient sensitizer for Mn$^{2+}$. Liu et al. prepared the Eu$^{2+}$- and Mn$^{2+}$-co-doped γ-AlON phosphors and investigated their photoluminescence properties. An appreciable overlap between the excitation spectrum of Mn$^{2+}$ and the emission spectrum of Eu$^{2+}$ is observed, and the energy transfer from Eu$^{2+}$ to Mn$^{2+}$ definitely occurs, leading to a 9 times improvement in luminescent intensity of Mn$^{2+}$, as shown in Fig. 10. Moreover, the external quantum efficiency (EQE) is increased from 7% to 49% with the Eu$^{2+} \rightarrow$ Mn$^{2+}$ energy transfer in γ-AlON, making γ-AlON:Mn$^{2+}$-Eu$^{2+}$ to be a suitable green phosphor excited by UV LEDs.

Ba$_2$LiSi$_7$AlN$_{12}$:Eu$^{2+}$.—Recently, “single-particle-diagnosis approach” is proposed by Xie’s group, which is an effective way to search for new phosphor hosts without fabrication of high-quality powder or single-crystal samples. Till now, several new phosphor systems have been discovered by this method, such as, blue-emitting Ba$_2$Si$_3$Al$_2$N$_{25}$:Eu$^{2+}$, yellow-emitting Ba$_3$Si$_{11}$Al$_2$N$_{23}$:Eu$^{2+}$, green-emitting Ba$_2$LiSi$_7$AlN$_{12}$:Eu$^{2+}$, blue-emitting Sr$_5$Si$_{6x}$Al$_{10}$O$_{23}$$_x$N$_{23}$:Eu$^{2+}$, and red-emitting (La$_{26-x}$Sr$_x$)Si$_3$O$_{11}$N$_{30}$:Eu$^{2+}$ phosphors. Among them, Ba$_2$LiSi$_7$AlN$_{12}$:Eu$^{2+}$, whose single particle is selected from the powder mixtures formed in the Ba$_3$N$_2$-Li$_3$N-Si$_3$N$_4$-AlN system, possesses interesting emission peaking at ∼515 nm with bandwidth as small as 61 nm.

As shown in Fig. 11, the green-emitting micro-crystal is found to be a new phosphor out of the many luminescent particles, and then its crystal structure is resolved via the super-resolution single-crystal X-ray diffraction. The analysis results show that the new phosphor has an orthorhombic unit cell of $a = 14.0993(2)$ Å, $b = 4.89670(10)$ Å, $c = 8.07190(10)$ Å, and $Z = 2$ with the $Pnnm$ space group (no.58).

Figure 9. (a) Mn K-edge XANES spectra of Mn compounds. a: γ-AlON:Mn-Mg, b: MnO, c: MnCO$_3$, d: Mn$_2$O$_3$, e: MnO$_2$, and f: Mn$_3$N$_2$; (b) Mn coordination structure in γ-AlON:Mn-Mg, tetrahedral model (8a site). Red: 32$e$ anion, orange: 8$a$ cation, blue: 16$d$ cation. (Reproduced with permission from Ref. 43, copyright 2012, Elsevier Science).

Figure 10. (a) Energy transfers from Eu$^{2+}$ to Mn$^{2+}$; (b) Comparison of photoluminescence spectra of γ-AlON:Mn$^{2+}$ (green), and γ-AlON:Eu$^{2+}$-Mn$^{2+}$ (blue). (Reproduced with permission from Ref. 45, copyright 2015, American Chemical Society).
channel along the b direction. Ba occupies the one-dimensional channel in a zigzag manner along the b direction. There is only one crystallographic site for Ba, which is coordinated by 11 N atoms, and the BaN$_{11}$ polyhedra are linked by face-sharing manner. The activator Eu is also coordinated by 11 N atoms, and the distance between Eu and N ranges from 2.86 Å to 3.24 Å with an average distance of 3.12 Å, as shown in Table I.

The temperature dependence of the emission spectra, peak intensity, and integrated intensity is displayed in Fig. 12b. At 200 and 300 °C, the peak intensities are 84 and 76% of the intensity observed at room temperature, whereas the integrated intensities are 95 and 91% of that at room temperature, respectively. The rigid condensed structure is one reason for the high thermal stability of this phosphor. Given the high internal quantum efficiency of 79% upon excitation at 405, this compound is characterized as a promising candidate for the backlighting displays.

Table I. Eu-N interatomic lengths (Å) in Ba$_2$Li$_2$(Al$_2$Si$_2$)N$_6$:Eu$^{2+}$.

| Bond name | Bond length (Å) | Bond name | Bond length (Å) |
|-----------|----------------|-----------|----------------|
| Eu-N$_2$  | 2.862(6)       | Eu-N$_3$  | 3.199(10)      |
| Eu-N$_3$  | 2.939(9)       | Eu-N$_4$  | 3.261(5)       |
| Eu-N$_5$  | 2.939(9)       | Eu-N$_4$  | 3.261(5)       |
| Eu-N$_5$  | 3.077(4)       | Eu-N$_4$  | 3.238(9)       |
| Eu-N$_5$  | 3.077(4)       | Eu-N$_4$  | 3.238(9)       |
| Eu-N$_5$  | 3.199(10)      | Eu-N$_4$  | 3.238(9)       |

Figure 11. Photographs of (a) a product generated from Ba$_2$N$_7$-Li$_3$N-Si$_3$N$_4$-AlN system and (b) the selected green luminescent particle. Crystal structure of Ba$_2$Li$_2$(Al$_2$Si$_2$)N$_6$:Eu$^{2+}$ (c) from the [010] direction and (d) from the [001] direction. (Si,Al)N$_4$ tetrahedral: blue; LiN$_4$ tetrahedral: red; BaN$_{11}$ polyhedral: green; Ba sphere: green; N sphere: white. (Reproduced with permission from Ref. 20, copyright 2015, American Chemical Society.)
Figure 12. (a) Photoluminescence spectra and (b) temperature dependent emission spectra of one Ba$_2$Li$_7$AlN$_{12}$:Eu$^{2+}$ particle. (Reproduced with permission from Ref. 20, copyright 2015, American Chemical Society).

thermal quenching and the emission intensity at 200°C keeps $\sim$70% of that at room temperature.

Narrow-Band Red Phosphors

Sr[Li$_3$N$_4$]:Eu$^{2+}$—Sr[Li$_3$N$_4$]:Eu$^{2+}$ is reported as a new narrow-band red phosphor, which exhibits a highly efficient red emission peaking at $\sim$650 nm with a FWHM of $\sim$50 nm, together with low thermal quenching ($\sim$95% relative to the quantum efficiency at 200°C). Later, facile synthesis methods have been investigated. The crystal structure of Sr[Li$_3$N$_4$]:Eu$^{2+}$ is solved and refined from single-crystal and powder X-ray diffraction (XRD) data, revealing a triclinic variant of the UCr$_4$C$_4$ structure type (space group $P\overline{1}$ (no. 2), $Z = 4$, $a = 5.86631(12)$ Å, $b = 7.51099(15)$ Å, $c = 9.96545(17)$ Å, $\alpha = 83.6028(12)^{\circ}$, $\beta = 76.7720(13)^{\circ}$ and $\gamma = 79.5650(14)^{\circ}$, and is isotypic to the oxoplumbate Cs[Na$_3$PbO$_4$].

Figure 13. Crystal structure of BaLi$_2$(Al$_2$Si$_2$)N$_6$. (Al/Si)N$_4$ tetrahedra (orange), Li (violet), Ba (red) with viewing direction of (a) [010] and (b) [001]; (c) Bisphenoidal arranged tetrahedral of Li$_2$N$_6$-units; (d) Truncated square pyramid of BaN$_8$; (e) Network typology with viewing direction [010]. (Reproduced with permission from Ref. 21, copyright 2015, American Chemical Society).
Table II. Ba-N interatomic lengths (Å) in Ba[Li2(Al2Si2)N6].

| Bond name | Bond length (Å) |
|-----------|-----------------|
| Ba-N1     | 2.934(18)       |
| Ba-N1     | 2.934(18)       |
| Ba-N1     | 2.934(18)       |
| Ba-N1     | 2.934(18)       |

Table III. Sr-N interatomic lengths (Å) in Sr[LiAl3N4].

| Bond name | Bond length (Å) |
|-----------|-----------------|
| Sr1-N5    | 2.690(10)       |
| Sr1-N1    | 2.691(10)       |
| Sr1-N4    | 2.727(11)       |
| Sr1-N8    | 2.741(11)       |
| Sr1-N7    | 2.797(12)       |
| Sr1-N6    | 2.930(12)       |
| Sr2-N7    | 2.974(12)       |

In Fig. 15 is presented a structural overview of Sr[LiAl3N4]:Eu2+. The crystal structure of Sr[LiAl3N4] is characterized as follows: (1) highly condensed and rigid framework of edge- and corner-sharing AlN4 and LiN4 tetrahedra with channels of vierer rings along [011]; (2) ordered distribution of AlN4 and LiN4 tetrahedra; and (3) cuboid-like SrN8 and the activator Eu2+ (1.25 Å) with almost the same size as Sr2+ (1.26 Å). There are two crystallographic Sr sites, each coordinated by eight N atoms (Sr-N: 2.69–2.91 Å) in a highly symmetric cuboid-like environment (see Table III). The SrN8 polyhedra are connected by common faces, forming endless strands along [011], with Sr-Sr distances of 3.27 Å.

Fig. 16a displays the excitation and emission spectra of the typical CaAlSiN3:Eu2+ and Sr[LiAl3N4]:Eu2+ red phosphors. Sr[LiAl3N4]:Eu2+ exhibits a broad absorption band with the maximum value at ∼466 nm. The emission spectrum peaks at 654 nm and exhibits an extremely narrow band (FWHM ∼50 nm), thus fitting well with the curve of human eye sensitivity. As the sensitivity curve of the human eye is very steep in the saturated red spectral range, even small changes in emission peak position and width have a great impact on the spectral lumen equivalent. Red phosphors with a deep-red emission peak position (Ca[LiAl3N4]:Eu2+, λem = 668 nm) or a broad emission band (CaAlSiN3:Eu2+, FWHM = 90 nm) show a large portion of emitted light outside the human eye sensitivity and a lot of energy is wasted. Therefore, red phosphors with emission maximum below 655 nm and a relative small FWHM are required for practical use. Moreover, Sr[LiAl3N4]:Eu2+ exhibits a higher color purity compared with the commercial red phosphor and could help to further increase the maximum accessible color gamut of LCD displays based LED backlighting. According to the absorption band of the host lattice, the optical bandgap is estimated to be 4.7 eV, which is in good agreement with the calculated bandgap of 4.6 eV. The emission spectra of Sr[LiAl3N4]:Eu2+ were recorded at different excitation wavelengths (Fig. 16b) and are consistent with the excitation spectra (Fig. 16a).

Figure 14. (a) UV/vis reflection spectrum, and (b) excitation (blue line) and emission (green line) spectra of Ba[Li2(Al2Si2)N6]:1 mol%Eu2+. (Reproduced with permission from Ref. 21, copyright 2015, American Chemical Society).

Figure 15. Structural overview of Sr[LiAl3N4]:Eu2+. (a) Perspective view with channels of vierer rings along [011]; (b) Strands of face-sharing cuboid-like SrN8 polyhedra coordinated by AlN4 and LiN4 tetrahedra; (c) Cuboid-like SrN8 polyhedra. Sr: yellow spheres, N: blue spheres, AlN4: blue tetrahedral, LiN4: red tetrahedral. (Reproduced with permission from Ref. 17, copyright 2014, Nature Publishing Group).
Figure 16. Photoluminescence properties of Sr[LiAl3N4]:Eu2+. (a) Excitation (Sr[LiAl3N4]:Eu2+: blue; CaAlSiN3:Eu2+: light gray) and emission (Sr[LiAl3N4]:Eu2+: pink; CaAlSiN3:Eu2+: dark gray) spectra. The dotted line indicates the upper limit of the human eye sensitivity; (b) Emission spectrum of Sr[LiAl3N4]:Eu2+ at 6 K with the vibronic structure of the emission transitions; (c) Temperature dependence of the relative integrated photoluminescence intensity (PLQE) for Sr[LiAl3N4]:Eu2+; (d) Temperature dependence of the spectral emission, showing a small shift toward higher energies with temperature. (Reproduced with permission from Ref. 17, copyright 2014, Nature Publishing Group).

accordance with the calculated value of (4.56 ± 0.25) eV. To further understand the origin of luminescent features, low-temperature measurements at 6 K are performed, as shown in Fig. 16b. Well-resolved vibronic structure of the emission transitions along with the zero phonon line energy $U_0$ at 15,797 cm$^{-1}$ are observed. The low number of vibronic structures in the high-energy tail of the emission band indicates a weak electron-phonon coupling of Eu$^{2+}$ in Sr[LiAl3N4]. Moreover, the Stokes shift of the luminescence is calculated to be as small as 956 cm$^{-1}$. Smaller Stokes shifts and thus narrower emission bands observed for Eu$^{2+}$ phosphors are commonly associated with a high symmetric dopant-site geometry.\textsuperscript{55} Owing to similar local electronic structure and comparable crystal-field splitting effects for both cuboidal coordination Sr sites, inhomogeneous line broadening of the emission band, resulting from different activator environments, is reduced to a minimum. This clarifies why, with two sites which can be occupied by the activator Eu$^{2+}$ ion, such a narrow emission band is still observed.

Fig. 16c shows the temperature dependence of the relative integrated photoluminescence intensity of Sr[LiAl3N4]:Eu2+. At 500 K, the integrated intensity drops by only 5%, demonstrating excellent thermal stability. The spectral emission changes at elevated temperature are shown in Fig. 16d. Notably, the emission band only shifts toward shorter wavelength side by $\sim$1 nm and broadens by 374 cm$^{-1}$ from 303 to 465 K. The Eu$^{2+}$ 5$d$ conduction band separation in Sr[LiAl3N4]:Eu$^{2+}$ is calculated to be as large as $\sim$0.28 eV, thus avoiding photoionization and keeping outstanding thermal stability at elevated temperature.\textsuperscript{56} Moreover, Sr[LiAl3N4]:Eu$^{2+}$ has been reported to be moisture-sensitive. Coating technology is a potential avenue for improving stability property that is needed for application in the LED industry. Liu et al recently improved the unstable Sr[LiAl3N4]:Eu$^{2+}$ by coating it with organosilica surfactants.\textsuperscript{57,58} The coated samples showed excellent moisture resistance while retaining an external quantum efficiency (EQE) of 70% of their initial EQE after aging for 5 days under harsh conditions. These results indicate that Sr[LiAl3N4]:Eu$^{2+}$ is an outstanding red-emitting candidate for backlighting applications with high color purity.

Sr[Mg3SiN4]:Eu$^{2+}$.—Novel nitridomagnesosilicate Sr[Mg3SiN4]:Eu$^{2+}$ is demonstrated to be the narrowest Eu$^{2+}$-doped red phosphor described in the literature so far with a FWHM
strong uniformity, which is beneficial to reduce inhomogeneous two enantiomeric strands of "cubes" per unit cell, linked by a SiN4 structure type (see Fig. 17a) and exhibits specific structural features. The "SrN8 cubes" are connected via face sharing with ones from the trans excitation spectrum shows two maxima at 560 nm. However, for practical use, the emission maximum is too red-shifted and should be below 650 nm to compete with other emission band peaking at 668 nm with a remarkably narrow FWHM of 62 nm.61 Both compounds are performed to crystallize at Sr2+ concentration increases significantly by cooling, and the temperature stability of Sr[Mg3SiN4]:Eu2+ leaves room for improvement. Fig. 18d displays the thermal quenching behavior of Sr[Mg3SiN4]:Eu2+ in comparison to Sr[LiAl3N4]:Eu2+. Surprisingly, despite of the smaller Stokes shift of Sr[Mg3SiN4]:Eu2+, it is the Sr[LiAl3N4]:Eu2+, not Sr[Mg3SiN4]:Eu2+, shows outstanding thermal stability. On the other hand, an estimated energetic separation between the lowest Eu2+ 5d state and the conduction band for Sr[Mg3SiN4]:Eu2+ is ~0.13 eV, whereas the Eu2+ 5d-conduction band separation in Sr[LiAl3N4]:Eu2+ is calculated to be ~0.28 eV.56 In other words, thermal photoionization, due to the low bandgap, seems most likely to be responsible for the significant thermal quenching of Sr[Mg3SiN4]:Eu2+. Modulation of the bandgap through cation substitution represents an effective means to improve the thermal stability.

Ca[LiAl3N4]:Eu2+ is isotypic with Sr[Mg3SiN4]:Eu2+ and also exhibits similar narrow-band red emission, as shown in Fig. 20. The excitation spectrum shows two maxima at ~485 and ~560 nm, respectively. Under 470 nm excitation, Ca[LiAl3N4]:Eu2+ yields an emission band peaking at 668 nm with a remarkably narrow FWHM of ~60 nm. However, for practical use, the emission maximum is too red-shifted and should be below 650 nm to compete with other commercially available phosphor materials.

\[
\text{Li}_2(\text{Ca}_{1-x}\text{Sr}_x)_2[\text{Mg}_2\text{Si}_2\text{N}_6]:\text{Eu}^{2+} \quad (x = 0 - 0.06) = \text{Li}_2\text{Ca}_2[\text{Mg}_2\text{Si}_2\text{N}_6]:\text{Eu}^{2+} \text{ and Li}_2(\text{Ca}_{0.8}\text{Sr}_{0.2})[\text{Mg}_2\text{Si}_2\text{N}_6]:\text{Eu}^{2+} \text{ are reported to reveal extraordinary emission characteristics with anarroid-band red emission peaking at 638 and 634 nm, respectively, and a bandwidth of 62 nm. Both compounds are performed to crystallize in the monoclinic space group C2/m (no. 12).}
\]

Crystal structures are solved and refined from single-crystal X-ray diffraction data (Z = 2, Li2Ca2[Li2Si2N6], a = 5.5472(11) Å, b = 9.844(2) Å, c = 5.9978(12) Å, β = 97.13(3)°;...
Figure 18. (a) UV/Vis-reflection spectrum of Sr\([\text{Mg}_3\text{SiN}_4]\), and the red line is drawn tangent to the slope of the reflectance curve; (b) Excitation (blue) and emission (red) spectra of Sr\([\text{Mg}_3\text{SiN}_4]\):Eu\(^{2+}\); (c) Low temperature emission spectra of Sr\([\text{Mg}_3\text{SiN}_4]\):Eu\(^{2+}\) between 6 and 300 K; (d) Thermal quenching data for the Eu\(^{2+}\) 5\(d\) → 4\(f\) emissions of Sr\([\text{LiAl}_3\text{N}_4]\):Eu\(^{2+}\) and Sr\([\text{Mg}_3\text{SiN}_4]\):Eu\(^{2+}\). (Reproduced with permission from Refs. 19 and 56, copyright 2014, 2016, American Chemical Society, Wiley).

Figure 19. Crystal structure of Ca\([\text{LiAl}_3\text{N}_4]\), with Al\(\text{N}_4\) tetrahedra (blue), Li\(\text{N}_4\) tetrahedra (red), and Ca atoms and Ca\(\text{N}_8\) polyhedra (orange). (a) Unit cell in projection along [001]; (b) Coordination of Ca\(\text{N}_8\) polyhedra; (c) Strands of face-sharing Ca\(\text{N}_8\) polyhedra with surrounding Li\(\text{N}_4\) tetrahedra. (Reproduced with permission from Ref. 18, copyright 2014, American Chemical Society).
Li$_2$(Ca$_{1.88}$Sr$_{0.12}$)[Mg$_2$Si$_2$N$_6$], $a = 5.5744(2)$ Å, $b = 9.8439(3)$ Å, $c = 6.0170(2)$ Å, $\beta = 97.252(1)^\circ$. The network of Li$_2$Ca$_2$[Mg$_2$Si$_2$N$_6$] is made up of edge-sharing double tetrahedra with the formula [Si$_2$N$_6$]$^{2-}$ that are interconnected by chains of edge-sharing Mg$_2$N$_4$ tetrahedra (see Fig. 21a). Ca/Sr atoms occupy the distorted octahedral voids coordinated by N. In the (Ca,Sr)N$_6$ octahedra the (Ca,Sr)-N$_1$ bonds are expanded by 0.014 and 0.008 Å via substituting Ca by 6% Sr ($x = 0.06$), and the (Ca,Sr)-N$_2$ bond lengths are summarized in Table V. Two Li atoms are also octahedrally coordinated by N (see Fig. 21c).

UV/Vis reflectance spectra of Eu$^{2+}$-doped and undoped samples of Li$_2$Ca$_2$[Mg$_2$Si$_2$N$_6$] are measured to determine the bandgap, as shown in Fig. 22a. The strong absorption band in the blue to yellow region with two maxima at $\sim 410$ and $\sim 460$ nm is attributed to the $4f^7 \rightarrow 4f^{6-n}5d^n$ absorptions in Eu$^{2+}$. The absorption band around 240–280 nm is ascribed to the host lattice absorption, and therefore the optical bandgap is estimated to be $\sim 4.6$ eV. The luminescence spectra of Li$_2$Ca$_2$[Mg$_2$Si$_2$N$_6$]:Eu$^{2+}$ and Li$_2$(Ca$_{1.88}$Sr$_{0.12}$)[Mg$_2$Si$_2$N$_6$]:Eu$^{2+}$ are displayed in Fig. 22b. The excitation spectra exhibit that the title compounds can be effectively excitable by UV to blue light. When excited, Li$_2$Ca$_2$[Mg$_2$Si$_2$N$_6$]:Eu$^{2+}$ and Li$_2$(Ca$_{1.88}$Sr$_{0.12}$)[Mg$_2$Si$_2$N$_6$]:Eu$^{2+}$ show luminescence in the red spectral range peaking at 638 nm and 634 nm, respectively, with small FWHM of $\sim 62$ nm. Although the Eu$^{2+}$ in title compounds are located in the distorted octahedral coordination just like Ca$_1$-Sr$_1$Al$_2$N$_4$:Eu$^{2+},$62 the host lattice ions Li, Mg, and Si all occupy distinct lattice sites instead of a statistical distribution over the same lattice site contributes to the smaller Stokes shifts, limited inhomogeneous broadening of the emission bands, and therefore narrow band emission. The introduction of Sr causes an enlarged Eu-N distance, and hence reduces the crystal field splitting. Finally, the excitation and emission maxima are shifted slightly toward short wavelengths.

### Table V. (Ca,Sr)-N interatomic lengths (Å) in Li$_2$Ca$_2$[Mg$_2$Si$_2$N$_6$] and Li$_2$(Ca$_{1.88}$Sr$_{0.12}$)[Mg$_2$Si$_2$N$_6$].

| Bond name | Li$_2$Ca$_2$[Mg$_2$Si$_2$N$_6$] (Å) | Li$_2$(Ca$_{1.88}$Sr$_{0.12}$)[Mg$_2$Si$_2$N$_6$] (Å) |
|-----------|--------------------------------|---------------------------------|
| Ca-N$_1$/[Ca,Sr]-N$_1$ (2x) | 2.494(2) | 2.508(1) |
| Ca-N$_2$/[Ca,Sr]-N$_2$ (2x) | 2.748(2) | 2.756(1) |
| Ca-N$_3$/[Ca,Sr]-N$_3$ (2x) | 2.523(2) | 2.524(1) |

### Summary and Outlook

The structural parameters and luminescent properties of the narrow-band phosphors reviewed in this article are summarized in Table VI. From the viewpoint of materials design, some underlying requirements for designing novel narrow-band phosphors have been analyzed as follows:

Firstly, a rigid and ordering network structure is very important to reduce lattice-phonon energies, and thus to inhibit nonradiative relaxation. For example, compared with ordered variants of the UCr$_4$C$_4$-structure type such as Ca[LiAl$_3$N$_4$]:Eu$^{2+}$, Sr[LiAl$_3$N$_4$]:Eu$^{2+}$, or Sr[MoSiN$_3$]:Eu$^{2+}$, the disordered UCr$_4$C$_4$-structure type compounds like Ca[Mo$_2$Al$_2$_N$_3$]:Eu$^{2+}$, Sr[Mo$_2$Al$_2$_N$_3$]:Eu$^{2+}$, Ba[Mo$_2$Al$_2$_N$_3$]:Eu$^{2+}$, Eu[Mo$_2$Ga$_2$_N$_3$]:Eu$^{2+}$, as well as Ba[Mo$_2$Ga$_2$_N$_3$]:Eu$^{2+}$ exhibit relative broad emission band. In these compounds, statistical distribution of the framework cations (here: Mg$^{2+}$ and Al$^{3+}$) leads to constantly varying distances (Al$^{3+}$/Ga$^{3+}$/Mo$^{6+}$)-N in the tetrahedrally coordinated positions, accompanied by a broad range of Eu-N bond lengths and environments. The differing crystal fields directly cause inhomogeneous line broadening of the emission band. Other examples, like Sr[Mo$_3$Ge$_2$N$_6$]:Eu$^{2+}$ and Ba[Mo$_3$Si$_2$N$_6$]:Eu$^{2+}$, also show broad emission because of the disordering of the tetrahedrally coordinated cations.$^{65}$

Secondly, only one single crystallographic site and almost the same size for the activator is another important precondition for reduction of inhomogeneous line broadening caused by different crystal fields. For example, (Ba,Sr)$_2$Si$_2$N$_4$:Eu$^{2+}$ shows two crystallographic sites that can be occupied by Eu$^{2+}$. As a result of the larger chemical differences of the representative sites, the emission maxima are distinct and thus lead to a relatively broad composite emission.$^{56,67}$ In fact, all the compounds reviewed in this article except Sr[LiAl$_3$N$_4$]:Eu$^{2+}$ have only one crystallographic site for the activator in the rigid network. As for Sr[LiAl$_3$N$_4$]:Eu$^{2+}$, both Sr sites are coordinated in almost identical spheres. Owing to comparable crystal-field splitting effects for both sites, inhomogeneous line broadening of the emission band, resulting from different activator environments, is reduced to a minimum.

Thirdly, a high symmetry around the activator site with a high coordination number, producing the same distance between the activator and ligand, is favorable for restricting inhomogeneous emission broadening. In other words, asymmetric dopant site geometry and smaller coordination numbers are commonly associated with pronounced structural relaxation, larger Stokes shifts and, thus, broader
emission bands. That is why compounds with cube-like coordination with longer activator-ligand lengths, such as Sr[LiAl3N4]:Eu2+, Sr[LiAl3N4]:Mn2+, Ba2LiSi7AlN12, and Sr[LiAl3N4]:Eu2+ exhibit a large barrier toward thermal ionization (>0.5 eV) and, hence, excellent thermal quenching stability. By contrast, the lowest Eu2+ 5d state and the conduction band of Sr[LiAl3N4]:Eu2+ is found to be only 0.13 eV, thus an inferior thermal stability.

Finally, it should also be pointed out that these rules are mainly suitable to rare-earth ions with 4f-5d transitions, e.g., Eu2+, but not activators having spin- or parity-forbidden electron transitions, such as Mn2+ or Mn3+.

Acknowledgments

We are grateful to the financial supports from the JSPS KAKENHI (no. 15K06448), National Natural Science Foundation of China (no. 51272259, no. 5157223, and no. 51472087), and National Postdoctoral for Innovation Talents.

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Table VI. Summary of the structural parameters of the narrow-band phosphors.

| Phosphor          | CN      | Bond length (Å) | λ_em (nm) | FWHM | Band gap (eV) |
|-------------------|---------|-----------------|-----------|------|--------------|
| β-SiAlON          | 9       | 2.49–2.83       | 535       | 55   | 7.2 ± 0.268  |
| γ-AlON            | 4       | 1.85            | 520       | 44   |              |
| Ba2LiSi12Al112    | 11      | 2.86–3.24       | 515       | 61   |              |
| Ba[Li2(Al2Si2N6)] | 8       | 2.93–3.10       | 532       | 57   | 4.6±2       |
| Sr[LiAl3N4]       | 8       | 2.67–2.97       | 650       | 50   | 4.7±2       |
| Sr[LiAl3N4]       | 8       | 2.65–3.29       | 615       | 43   | 3.9±2       |
| Ca[LiAl3N4]       | 8       | 2.52–2.91       | 668       | 60   |              |
| Li2Ca2[Li2Ca2Al2Si2N6] | 6 | 2.49–2.52       | 638       | 62   | 4.6±4       |

Figure 22. (a) UV/vis reflectance spectra of undoped (red line) and doped (blue line) spectra of Li2Ca2[Li2Ca2Al2Si2N6]:Eu2+ (ex: dark blue line, em: orange line) and Li2[Ca1.88Sr0.12][Li2Ca2Al2Si2N6]:Eu2+ (ex: light blue line, em: red line). (Reproduced with permission from Ref. 61, copyright 2017, American Chemical Society.)
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