Review—Narrow-Band Emission of Nitride Phosphors for Light-Emitting Diodes: Perspectives and Opportunities

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Searching for narrow-band red-emitting and thermally stable phosphors is the ultimate strategy toward enhanced performance of phosphor converted light emitting diodes (pc-LED). The red emission is assured by the nitride host because of its relatively more covalent character than oxides and sulfides; however, the narrow emission is attributed to crystallographic, morphological, and electronic considerations. The syncretic coordination site ensures equal ligand effect in all direction fits well with the configuration of Eu3+ f orbitals in the excited state, as observed in cuboid nitrates. Further, thermal stability is ascribed not only to suitable bandgap but more specifically, a relatively distant location of the lowest 5d level from the bottom of the conduction band (CB) that consequently entails high energy to quench excited electrons by exciting them further up to the CB. Modes toward the development of new nitride hosts with potentially narrow-band emission have been identified. A viewpoint on light-emitting diode (LED), backlighting, and laser lighting, which remains the most economically-rewarding phosphors application, is presented. Other existing frontiers, such as agricultural illumination and persistent luminescence, maximize nitride systems that have other properties other than the stringent narrow-band red emission and excellent thermal stability required for the desired improvement of the mainstream LED application. © The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0161801jss] All rights reserved.

The discovery, development, and commercialization of phosphors are expected to satisfactorily fare with the benchmark set for phosphor converted-LEDs. First, the excitation wavelength of the phosphors must be compatible with the blue LED pump, thereby emitting the desired colors and consequently generating white light. Second, the quantum efficiency should be high. Third, phosphor must have a high absorption rate in the LED range, which technically narrows the choices to those that are excitable through 4f → 5d, d → d, np → nd, and ns → np transitions. Fourth, it must have high thermal quenching ability. Fifth, the inherent stability against moisture and continuous irradiation ensures the durability and longevity of the device. Sixth, a rational design must be presented for the synthesis conditions from the selection of starting materials, synthesis strategy, and costs to allow the smooth cross-over to eventual industrial-scale production.1,2

Tuning the phosphor photoluminescence requires a tunable phosphor and a set of strategies to introduce changes in intensity, emission wavelength, and full width at half-maximum (fwhm). Moreover, the following are of paramount consideration in tuning the phosphor photoluminescence. First, a clear understanding of crystal and local structures and the investigation of appropriate structural models, which includes bandgap and crystal engineering. Second, the tuning of chemical composition for a given phosphor can be with the selected dopant, changes in the cation, or solid solution that alters the overall structural framework. The f-d transition Eu3+ and Ce3+ can be altered by varying the crystal field strength, which redounds to varying emission peak positions. Through cation or anion substitution, a bathochromic or hypsochromic shift may be achieved.4,5 For example, by bypassing the geometrical restriction of the activator by replacing a few elements in the lattice.6 Last, the design of the energy transfer process, wherein the tunable ion-to-ion interaction emission expands the colorway of phosphors.

By tuning the relative amount of phosphor component, generating a continuous emission spectrum akin to the black body radiation at the corresponding correlated color temperature (CCT) over the entire range is possible. However, high color rendering index (CRI) which is usually above 90 is required to ensure the most natural color rendition, thereby sacrificing the luminous efficacy of radiation (LER). Considering the eye sensitivity curve, light beyond 650 nm is poorly received by the human eye and is detrimental on the luminous efficacy, which is also known as the infrared (IR) spillover.8 Thus, finely tuning the peak wavelength and width of the emission spectrum with particular attention to the red emitter is important to consider the human visual perception for pc-LED emission.9

Human vision and color perception.—The human eye parameterizes the key concepts that define, approximate, and evaluate the illumination quality. Complementing these concepts are energy efficiency and stability evaluations that jointly create the requirement checklist of an efficient light-emitting device. The human eye receives light through the pupil, passing through the lens and projects to the retina (Fig. 1). The retina is lined with photoreceptors known as rods and cones. Rods are responsible for dark and bright vision, as well as peripheral vision. The cones which are concentrated in the fovea, a small groove in the retina, are sensitive to short, medium, and long wavelengths (Fig. 1), and thus given the names blue, green, and red cones, respectively. This labeling means that color is defined by how the cones are activated and their composite reaction to photosensitization, which allows the conversion of light to chemical signals that are sent to the brain where interpretation takes place.

As such, the sensitization of the three cones was translated into the Commission Internationale de l’Eclairage (CIE) standard observer in 1931. Three colors have then been transformed in a convenient 2D plot, where x and y define a color (Fig. 2a). The edge of the diagram represents pure colors, as well as the triangle formed by blue (460 nm), green (540 nm), and red (680 nm). The area inside the triangle is technically what the eyes are capable of perceiving.

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Thus, any color may be expressed in three primary colors and would correspond to a point in the diagram. Generating white color emission, which is located in the middle of the chromaticity diagram, requires the combination of three colors; thus, the red, green, and blue (RGB) expression in display science and technology has become important.

Light quality.—The light quality from an illumination device can be simply evaluated by its intensity and accuracy. As earlier premised, these criteria respond to the ability and limitation of the human eye. A light source is primarily used to illuminate, and brightness is therefore the basic requirement. The intensity of the light-emitting device would thus refer to the source brightness perceived by the naked eye and expressed in lumen per watt (lm/W), otherwise known as the LER. The LER pertains to how efficiently a given amount of power (1 lumen) is converted to light, which is practically quantified from the emission spectrum. This is scaled with the eye sensitivity which peaks at 555 nm in the green region (Fig. 2b). When 100% electrical power is converted into light at 555 nm, the efficiency of the light source would be equal to 683 lm/W. As this is the peak, and other wavelengths would have low LER to approximately 350 lm/W due to the diminishing eye sensitivity on both sides of the curve because red and blue are also necessary for white light, thereby suggesting a compromise of LER and color quality. The eye sensitivity to bright light condition is referred to as photopic vision. As light dims to around 1 cd/m², the rods sensitivity are at 504 nm and shifts the eye to night mode or scotopic vision, which also refers to the sensitivity of the eye under dim conditions.

Aside from sufficient intensity (brightness), the accuracy of the light source to reproduce colors or its color rendering capability is the other half of the light quality requirement. Color rendering is a relative description that depends on a standard. Thus, the standard selection plays a crucial role in the accuracy, reliability, and universality of the described output of a light-emitting device. The temperature of a
black body radiation at the point when it closely matches a test source is referred to as the CCT of the test source (Fig. 2c). If this value of the CCT is lower than 5000 K, then the color rendering index is determined from the black body radiator of the same CCT. In cases where the CCT value is above 5000 K, the proposed D65\textsuperscript{15} standard illuminant by the CIE is employed.

Color test samples are identified, and these samples comprise the battery of colors that are rated and weighted with regard to their reproducibility (Fig. 2d). The first eight are used to express the color rendering index, \( R_7 \) and \( R_9 \) is separately quantified as with the specific reproducibility (Fig. 2d). The first eight are used to express the color rendering index, \( R_7 \), \( R_9 \) is separately quantified as with the specific reproducibility (Fig. 2d). The first eight are used to express the color rendering index, \( R_7 \), \( R_9 \) is separately quantified as with the specific reproducibility (Fig. 2d). The first eight are used to express the color rendering index, \( R_7 \), \( R_9 \) is separately quantified as with the specific reproducibility (Fig. 2d).

Towards white-LED.—Guided by the RGB idea, its combinations result in the generation of white light. General strategy and approaches by which white LED is obtained also exist as shown in Fig. 3. The integration of three LEDs separately emitting RGB, or the single LED employed one or a combination of two or more phosphors; hence, the term phosphor-converted LEDs (pc-LED).\textsuperscript{12,16,17} The pc-LED approach is the prevailing configuration of most commercially available phosphors. For a long period, white light was based on a blue LED that excites YAG:Ce\textsuperscript{3+} to generate white light. Further, two phosphors (green and red) can be employed, thereby enhancing the red emission region, as well as the \( R_a \) and \( R_9 \). Also, gaining momentum is the complete use of phosphors as emission source after excitation with near ultraviolet LED (NUV-LED).\textsuperscript{18} A blue or NUV-excited white LED also has pros and cons in efficiency and performance.\textsuperscript{12,17}

Phosphors.—Central to the performance, application, and prospects of pc-LEDs is the type and quality of phosphor used. Classical inorganic phosphors consist of a host lattice with an activator ion doped in small amounts. These activators possess energy levels that can be occupied by excitation or indirectly by energy transfer, which gives rise to the characteristic luminescence upon relaxation.\textsuperscript{19} In the selection of phosphors, several properties need to be satisfied, such as the appropriate emission peak position and breadth, a compatible excitation spectrum, physical and thermal stability, and quantum efficiency.

Lanthanides are most commonly employed as activators, and the 4f-5d transitions define their excitation and emission profiles.\textsuperscript{21} However, these transitions are affected by crystal structure and local domains of the host because the intensity, peak position, and breadth are collectively tuned by their host. The 5d orbitals, which represent the excited state of these elements, is vulnerable to the structure of the host, coordination site symmetry, polarizability of anions, and the anionic framework covalence. Inherently, with Eu\textsuperscript{2+} or Ce\textsuperscript{3+} in a crystal host, the 4f to 5d levels are separated by energies spanning at most of the UV energy range. Owing to two critical factors, namely the crystal field splitting (CFS) and the nephelauxetic effects (NE) (Fig. 4a), the energy difference may be reduced to approach the near UV and blue wavelength range, thereby making these materials very suitable for the current blue and NUV-LEDs design.\textsuperscript{16} The crystal field splitting, \( D_{q} \), quantifies the highest and lowest \( d \) orbital splitting. This splitting is influenced by a variety of structural, electronic, and morphological features.\textsuperscript{22,23} In the coordination environment of the activator, a short bond length would mean that the anion in the first coordination shell is near to the activator. Hence, a strong interaction would lead to a large CFS, thereby stabilizing at a low level the lowest \( d \) level and thus, the effective energetic difference with the ground state (4f) becomes small, resulting in the redshift. In addition, NE, \( \beta \) contributes further to the stabilization of \( d \) orbitals as compared to its free ion state. This factor similarly depends on the anion (\( h \)) and the metal (\( k \)). Moreover, the energy stabilization is attributed to the reduced electronic repulsion due to the expanded electronic cloud accommodating the

![Figure 3](https://example.com/figure3.png)  
Figure 3. Various Phosphor-converted white light emitting diode design; (a) Yellow phosphor excited by blue LED; (b) Red and green phosphors excited by blue LED, and; (c) Red, green and blue phosphor excited by UV or NUV LED.

![Figure 4](https://example.com/figure4.png)  
Figure 4. (a) Crystal field splitting and nephelauxetic effects; (b) Stokes and anti-Stokes shifts; (c) Band gap and the relative positions of the 4f-5d transitions as in Eu\textsuperscript{2+}.
The reduction of the electronic repulsion and the increase in h value is attributed to covalency. Thus, the NE is related to covalency, wherein a high level of covalency results in a more significant centroid downshift effect. Apart from the two major factors, the Stokes shift, coordination geometry, distortions, and disordering also have effects on the 4f-5d energy level and could spectrally manifest.23

Thermal stability is another important property of phosphor. Heat is generally detrimental to luminescence and efficiency and will enable a shift in the emission peak position, as well as a decline in intensity.22 This finding could be ascribed to how the Eu lowest d orbital level is positioned with respect to the bottom of the CB (Fig. 4b). Heat could be sufficient to excite electrons in the d orbitals to the CB, thereby thermally quenching the emission through non-radiative modes and adversely affecting color, efficiency, and overall device performance.26,27

Based on a spectral pc-LED model with red and green phosphors, the target discovery and improvement toward narrow-band phosphors exemplify the optimization of conversion efficiency (CE) as predicated by bandwidths and peak positions, where CE refers to the lm/W rating. CE is calculated based on the luminous efficacy of radiation (LER) and Stokes loss. As revealed in Figs. 5, the desired developments are attained by reducing the bandwidth of the red phosphor. For example, given a device that yields the following: CCT = 3000 K, CRI with Ra > 90, R9 > 50, and an fwhm of 110 for red and green, the CE is 239. However, when the fwhm is reduced to approximately 30 nm, CE is further increased to 291 lm/W, accounting for the approximately 22% increase.10

**Figure 5.** (a) Improvement in lm/W as a function of the fwhm of the green and red phosphor components;10 (b) Classes of narrow-band emitting nitrides phosphors.

### Narrow-Band Nitride Phosphors

The robust structural diversity gives rise to unique and interesting physicochemical attributes that make nitrides as well as (oxy) nitrides take on a myriad of uses across various human need and consumption aspects.28-35 The remarkable optical properties are ascribed to its electronic band structure that can be tailored by altering its chemical composition, thereby allowing the development of exciting optical materials.36 The ionic-covalent nitrides where nitrogen-(non-metal) bonds is dominant, and the non-metal associated with N occupy interstitial spaces in the nitrogen framework. The bonds are considerably influenced by the element bonded to N. The luminescent nitrides belong to this class.36 Nitrogen has less electronegativity than oxygen, thereby rendering nitrogen-nitrogen bonds more covalent, which results in increased NE.37,38 Further, the formal charge of N (3-) renders the crystal field splitting more pronounced. The consolidated effect of these properties stabilizes the rare metal ions 5d orbitals, thereby affording emission in the long wavelength region.39,40

Mainstream nitride phosphors (Ba,Sr)2Si2N4:Eu2+ and (Ca,Sr)AlSiN3:Eu2+ possess several desirable properties, such as tunable albeit broad emission band, good thermal behavior, and high efficacy. However, the broad emission bands in the red spectral region ensure high CRI, but are highly detrimental to the luminous efficacy because a significant part of the emission band could span up to the 700 nm region, which is already beyond what the human eye could perceive. Hence, the need for narrow red emitting phosphors has indeed become even more compelling.

An unprecedented development of a novel set of nitride systems based on the UCr4C4 structure type has been introduced by an earlier report of the same type of isoelectronic and isotypic systems nearly a decade ago.14 However, their optical properties were not mentioned, and in depth investigations regarding their photoluminescence properties did not exist. The narrow-band red-emission of these materials and the shared cube-like activator site has earned the spotlight for these new set of phosphors while gaining insight on how to design and ensure narrow-band emissions, particularly in the red spectral region (Fig. 5b).

**Cuboid nitride.**—M[LiAl,N2]:Eu2+ (M = Ca, Sr). Dubbed as the next-generation phosphor, red-emitting Eu2+ -activated Sr[LiAl,N2] (SLA) nitridolithoaluminate phosphor was prepared from LiAlH4, AlN, SrH2, and EuF3 radiofrequency furnace (1 h at 1000 °C).41 This new material is blue light excitable (approximately 466 nm), has a narrow fwhm (approximately 50 nm) and red-emission band (650 nm) (Fig. 6a), and considerable high luminous efficacy and color rendition (CRI > 90). The two Sr crystallographic sites, each coordinated by eight N atoms in a highly symmetric cuboid environment, are the structural features responsible for the narrow-band emission. As the ionic radii of Sr2+ (1.26 Å) and Eu2+ (1.25 Å) dopant are nearly similar, the latter can replace Sr2+ ions in the lattice. The introduction of nitrogen in classical (oxo)aluminates systems is responsible for the high condensation degree, high thermal stability of the material, high rigidity of the host lattice, and limited local structural relaxation of the Eu2+ site in its excited state, which results in small Stokes shift and narrow-band emission.41 After the 440 nm excitation, the external and internal quantum efficiencies of SLA are approximately 52% and 76%, respectively. This red-emitting phosphor shows a 14% increase in luminous efficacy and excellent color rendition compared to the commercially available (Ba,Sr)2Si2N4:Eu2+. With the temperature-dependent photoluminescence intensity of SLA (Fig. 6b),25 the integrated light output drops by only 5% at 500 K compared to the Ce3+-doped garnet phosphors, and the change in chromaticity with temperature is low. In the temperature range of 303 to 465 K, the emission band shifts by only approximately 1 nm toward high energies while the spectrum broadens by approximately 374 cm⁻¹. This phosphor shows low fluctuations of the local activator chemical environment as compared to other phosphor materials, such as (M2)Si2N4:Eu2+ (M = Ca, Sr, Ba) or MsAlN3:Eu2+ (M = Ca, Sr).

SLA can satisfy the requirements for a red emitter illumination grade and high-power pc-LED applications and shows superior emission properties, high thermal quenching temperature (>95% relative quantum efficiency at 200 °C), high color rendition, and very satisfactory luminous efficacy. The Ca-variant of SLA, the red-emitting nitridolithoaluminate, and Ca[LiAl,N2]:Eu2+ phosphor are also prepared from a mixture of AlF3, LiN3, EuF3, and metallic Ca in an
The Ca[LiAl11N12]:Eu2+ phosphor consists of a highly-condensed rigid framework of AlN and LiN tetrahedra with Ca atoms positioned in the vierer ring channels along [001]. In Ca[LiAl11N12]:Eu2+, the Eu2+ activator occupies the Ca site, and this phosphor material shows red luminescence upon blue light excitation (Fig. 6c). When excited at 470 nm, the activator emits at 688 nm with fwhm of approximately 60 nm. The excitation spectrum shows two maxima at 485 and 560 nm. In comparison to (Sr,Ba)2Si5N8:Eu2+, the Eu2+ emission band. A good absorption in the blue to green spectral region makes this phosphor material suitable for pc-InGaN LEDs. Once in its excited state, the high condensation degree of this phosphor makes it appropriate for application in warm white lighting.

Figure 6. (a) Excitation (blue: SLA; light gray: CaAlSiN3) and emission of SLA (pink: SLA; dark gray: CaAlSiN3). Dotted line: upper limit sensitivity of the human eyes; (b) Temperature dependence of relative integrated PL intensity of SLA; (c) Excitation and emission spectra of Ca[LiAl11N12]: Eu2+. Reprinted with permission from Refs. 41,42. Copyright 2014 American Chemical Society.

Figure 7. (a) Normalized emission spectra at T = 300 K and T = 7 K of M[MG2Al2N12]:Eu2+ (0.1% Eu2+, M = Ca, Sr, Ba); (b) Temperature-dependent emission intensity of M[MG2Al2N12]:Eu2+; (c) Low (7 K) and high (300 K) temperature photoluminescence for M[MG2Al2N12]: Eu2+ (0.1% Eu2+, M = Ca, Sr, Ba). Reprinted with permission from Ref. 43. Copyright 2014 American Chemical Society.
Figure 8. (a) Excitation and emission spectra of Sr[Mg3SiN4]:Eu2+ (2 mol%); (b) Excitation and emission spectra of Ba[Mg3SiN4]:Eu2+ (black: 0.5 mol%; red: 2.5 mol%). Reprinted with permission from Refs. 44, 45. Copyright 2014, 2015 American Chemical Society.

to approximately 900 cm\(^{-1}\) (approximately 33 nm).\(^4^4\) The emission intensity of this phosphor significantly increases by cooling, and the relative quantum efficiencies close to 100% are attained at low temperatures. In contrast to SLA, the Sr[Mg3SiN4]:Eu2+ has blue-shifted emission and the narrowest among these cuboidal systems.

The nitridomagnesosilicate Ba[Mg3SiN4]:Eu2+ phosphor does not share the same crystal structure as the Sr variant. This phosphor was also prepared by solid state reaction of BaF2, Mg3N2 and Si(NH)2, LiN3 and EuF3. The excitation and emission spectra of Ba[Mg3SiN4]:Eu2+ are shown in Fig. 8b.\(^4^5\) The Ba[Mg3SiN4]:Eu2+ phosphor can be efficiently excited by blue light, and the excitation spectrum shows a broad band with a maximum at 465 nm. Excitation at 450 nm results in an emission in the red region centered at 670 nm with fwhm approximately 1970 cm\(^{-1}\). As the dopant concentration is increased to 2.5 mol%, further shift was observed in the emission maximum toward 680 nm while the emission width remained unaffected. At low temperature, the emission maximum of this phosphor is red-shifted by approximately 220 cm\(^{-1}\), and the degree of the Ba[Mg3SiN4] phosphor doped with 0.5 mol% Eu2+ is 32%.\(^4^5\)

Sr4LiAl11N14:Eu2+. The narrow-band red phosphor is just the third to be reported in the family of nitridolithoaluminates after SrLiAl3N4 and CaLiAl3N4. The synthesis approach involving non-stoichiometric amount of Li compensating any loss in open system solid state reaction (1400°C, 15 mins) provided a pink powder. The disordered AlLiN4 and AlN tetrahedra are connected by common corners and edges forming a rigid, highly-condensed framework. This tetrahedra also possessed four- and five-membered channels, and the single Sr crystallographic site is situated on the latter. These five-membered sites are formed by corner-sharing AlN4 and two (AlLi)N4 tetrahedra (Fig. 9a). Interestingly, a cuboid-like coordination formed by eight N atoms can be found inside this five-membered site. This cuboid-like coordination is UV and blue light excitable (460 nm) and emits at 670 nm with fwhm approximately 85 nm (Fig. 9b).\(^4^6\)

BaLi2(Al2Si2)N6:Eu2+. Another cuboid-like narrow-band emission in the green spectral region is BaLi2(Al2Si2)N6, which was prepared in the radiofrequency furnace using fluoride starting materials (AlF3, EuF3, BaF2). Also, Li and Si sources were separately prepared. This band features a cuboid-like coordination site for the single crystallographic Ba site. This truncated square pyramid is eight N coordinated and is shared with the cuboid nitrides showing narrow-band emission (Fig. 10a). At 1 mol% Eu2+ doping and upon blue light excitation, the phosphor emission at 532 nm is approximately 57 nm. The thermal-dependent emission revealed approximately 70% of the original intensity which is retained at 200°C (Fig. 10b).\(^4^7\)

“Symmetric” coordination nitride phosphors.— Ca\(_{4.75}\)Li\(_{10.5}\)Al\(_{10}\)N\(_{30}:\)Eu\(_{2+}\). These phosphors are dubbed as supertetrahedron phosphor, which belong to the hardly explored class of nitridoaluminates. The unusual crystal structure comprising sphalerite-like T5 supertetrahedra, which are composed of tetrahedral
AlN₄, and are interconnected by additional AlN₄ moieties. The network charge is compensated by Ca and Li ions (Fig. 11a). This phosphor has a highly efficient narrow-band red-emission centered at λ<sub>em</sub> = 645 nm and fwhm of approximately 1280 cm<sup>-1</sup> (approximately 58 nm) (Fig. 11b).<sup>48</sup>

Li₂(Ca₁₋ₓSrx)[Mg₂Si₂N₆]:Eu²⁺. The narrow-band re-emission, which is prepared through solid-state metathesis reaction, makes the parent nitridomagnesosilicate particularly interesting. An edge-sharing double tetrahedra ([Si₂N₆]<sup>10⁻</sup>) network is linked through chains edge-sharing MgN₄. Sr can be doped up to a maximum of approximately 6 mol%, which is sufficient to change the coordination polyhedron. Structurally, three Ca sites exist: trigonal prismatic (CN = 6) and two distorted octahedral (CN = 8). Although Eu can occupy all the sites, emission is only through the distorted octahedron (Fig. 12a). This phosphor lacks the desired cuboid coordination site; however, its distorted octahedral coordination proves to be effective in providing a narrow red emission of approximately 62 nm. The phosphor is blue-light (460 nm) excitable with emission peaking at 638 nm (Fig. 12b). Changing Ca with Sr revealed a slight blueshift due to the large Sr radius compressing the sites, thus leading to an increase in emission. Compared to a cuboid site, an octahedral site provides for increased local structure coordination, thereby resulting in a slightly broad yet still narrow emission band. The optical bandgap is approximately 4.6 eV and the internal quantum efficiency is 50%.<sup>49</sup>

Ba₂Li₆Si₇AlN₆:Eu²⁺. The narrow-band green-emitting phosphor was discovered by the single particle diagnosis technique. This phosphor was built upon corner-sharing (Si, Al)N₄, corrugated sheet, edge-sharing (Si, Al)N₄ and LiN₄ tetrahedra (Fig. 13a). The single crystallographic Ba site is spread in a zigzag arrangement in 1D channels. The coordination site is organized with 11 N and forms a polyhedral

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**Figure 10.** (a); (b) Excitation and emission profiles of Ba(Li<sub>2-x</sub>Mg<sub>x</sub>)(Al<sub>2+x</sub>Si<sub>2-x</sub>)N<sub>6</sub> where the blue and light blue is the excitation, and the green and orange are the emissions corresponding to x = 0.2 and x = 0.4, respectively (Inset: Cuboid-like, 8-N coordinated Ba site); (c) Thermal-dependent luminescence (Inset: Crystal structure). Reprinted with permission from Ref. 47. Copyright 2015 American Chemical Society.

**Figure 11.** (a) A detail of the Ca<sub>18.75</sub>Li<sub>10.5</sub>Al<sub>39</sub>N<sub>55</sub>:Eu²⁺ crystal structure showing the Ca2 site coordinated trigonal prismatically by N (light green polyhedron) which is different from the Na coordination (red polyhedral). The trigonal antiprismatic Ca1-N6 polyhedron sphere is the solid yellow polyhedral. (b) Excitation, reflectance, and emission (λ<sub>exc</sub> = 390 nm) spectra. Reprinted with permission from Ref. 48. Copyright 2016 American Chemical Society.
Figure 12. (a) Crystal structure of Li$_2$(Ca$_{1-x}$Sr$_x$)[Mg$_2$Si$_2$N$_6$]:Eu$^{2+}$ where the Mg tetrahedra (orange) forms linear face-sharing structure sandwiching Si tetrahedra (turquoise). The cations Ca/Sr and Li are denoted by the red and lilac spheres, respectively; (b) Excitation and emission bands of $x = 0$ and $x = 0.07$ from the emission of Eu$^{2+}$ in a distorted octahedral site. Reprinted with permission from Ref. 49. Copyright 2017 American Chemical Society.

that affords a narrow-band emission. Interestingly, the distance of one Ba to another, where the 3.12 Eu–N distance is at an average. The distance of Eu to a Ba site that emits green luminescence is approximately 0.2 Å. This site is efficiently excitable by UV (400 nm) light and emits at 515 nm with an fwhm of 61 nm. The IQE is 79%. Powder synthesis is at 1700°C with approximately 80% purity and a slight increase in fwhm (66 nm) (Fig. 13b).  

Ba$_3$Ga$_3$N$_5$:Eu$^{2+}$. The first nitridogallate that hosts the parity-allowed emission of Eu$^{2+}$ emission was prepared from elemental starting materials, with Na as flux and weld-shut Ta ampule is heated in a tube furnace to 760 nm for 48 h to afford a light orange powder.  

This compound is UV excitable and has a maximum emission intensity at 638 nm with fwhm approximately 84.7 nm (Fig. 14a). The basic structural motif is based on three edge-sharing tetrahedra structures built by GaN$_4$ tetrahedra connected to another unit running in the opposite direction, forming chains while forming three rings (Figs. 14b, 14c). This resulted in a high degree of condensation (approximately 3:5) as a manifestation of the dominance of edge-sharing arrangement over corner-sharing, and where no N is terminally linked to any Ga.

As in the case of the double nitride Mg$_3$Ga$_3$N$_5$, which is a yellow-orange emission centered at 578 nm, bears an octahedral site for doping. Even though the band is relatively broad at 132 nm, it prepares the way for double nitrides (in contrast to nitridogallates, which have an anionic Ga-containing framework) as potential hosts.  

Ba$_3$Si$_3$N$_2$O$_2$:Eu$^{2+}$. The MSi$_2$N$_2$O$_2$ ($M = $ Ca, Sr, Ba) family has been the subject of numerous investigations and intellectual property protection. However, the BaSi$_3$N$_2$O$_2$ has become particularly engaging because of its narrow emission and small Stokes shift.  

BaSi$_3$N$_2$O$_2$ possesses a layered structure with only one Ba and Si site. This structure is primarily defined by vertex-sharing SiON$_3$ tetrahedra, where N connects three silicon centers and O is the terminal. The alternating down and up arrangement forms a highly condensed silicate layer. These silicate layers are arranged by rotation at approximately 180° forming a cuboid-like arrangement around the Ba atoms that delineate them. SrSi$_3$N$_2$O$_2$ shared this arrangement of the silicate network with BaSi$_3$N$_2$O$_2$, except that it is tilted opposite to each other. By contrast, although CaSi$_3$N$_2$O$_2$ shared a distorted prism site for the cation, a more different arrangement was observed (Fig. 15a). The stacking disorder in BaSi$_3$N$_2$O$_2$ has the tendency to generate stacking domains that appear energetically similar. The observed blue-shifted emission of Ba as the cation is changed when Sr emerged from the evolution of the cuboid coordination site from a trigonal prism (as in Ca and Sr) driven by the large ionic Ba radius (Fig. 15b).  

The Ca and Sr excitation profiles are more akin to each other than that of Ba, while the emission bands move toward more blue from Ca to Sr to Ba. The narrowest emission is that of Ba (fwhm approximately 36 nm) with an excitation at 380 nm and an emission at 494 nm (Figs. 15b, 15c; Table I).

Figure 13. (a) The crystal structure of Ba$_2$Li$_5$Si$_7$Al$_2$N$_8$. The Si,Al (blue) and Li (red) tetrahedra create the 11-N coordinated Ba site; (b) Excitation and emission spectra that shows a narrow (fwhm $\sim$ 66 nm) green emission (515 nm) after 400 nm excitation. Reprinted with permission from Ref. 50. Copyright 2015 American Chemical Society.
Figure 14. (a) Emission of Ba₃Ga₃N₅ at 638 nm after UV excitation; (b) Four Ba crystallographic sites; (c) Crystal structure of Ba₃Ga₃N₅ showing the highly condensed GaN₄ tetrahedra (green) and the Ba (yellow spheres). Reprinted with permission from Ref. 51. Copyright 2012 American Chemical Society.

Figure 15. (a) Crystal structure of Ca, Sr, and Ba coordinated Si₂O₂N₂; (b) Spectral shift with Ca and Ba substitution on SrSi₂O₂N₂; (c) Relative peak position of Ca, Sr, Ba cation in [Si₂O₂N₄]²⁻ lattice. Reprinted with permission from Refs. 54, 57. Copyright 2014, 2009 American Chemical Society.
Table I. Structural properties of narrow-band nitride phosphors.

| Phosphor                | Activator | $\lambda_{\text{ex}}, \text{nm}$ | $\lambda_{\text{em}}, \text{nm}$ | Shape of coordination site | # of sites | fwhm, nm | Ref. |
|-------------------------|-----------|---------------------------------|---------------------------------|----------------------------|------------|---------|------|
| SrLiAl$_3$N            | Eu$^{2+}$ | 440                             | 650                             | cuboid                     | 2          | 50      | 41   |
| CaLiAl$_3$N$_4$        | Eu$^{2+}$ | 470                             | 668                             | cuboid                     | 1          | 60.3    | 42   |
| CaMg$_2$Al$_2$N$_4$    | Eu$^{2+}$ | 440                             | 607                             | cuboid                     | 1          | 66.9    | 43   |
| SrMg$_2$Al$_2$N$_4$    | Eu$^{2+}$ | 440                             | 612                             | cuboid                     | 1          | 68.3    | 43   |
| BaMg$_2$Ga$_2$N$_4$    | Eu$^{2+}$ | 450                             | 649                             | cuboid                     | 1          | 91.3    | 43   |
| SrMg$_3$Si$_3$N$_4$    | Eu$^{2+}$ | 460                             | 615                             | distorted cuboid           | 1          | 43      | 44   |
| BaMg$_5$Si$_3$N$_4$    | Eu$^{2+}$ | 450                             | 670                             | cuboid                     | 1          | 88.4    | 45   |
| Sr$_4$Li$_6$Al$_9$N$_{14}$ | Eu$^{2+}$ | 460                             | 670                             | cuboid                     | 1          | 85      | 46   |
| Ba$_2$[Li$_3$(Al$_3$Si$_5$N$_4$)] | Eu$^{2+}$ | 400                             | 532                             | distorted cuboid           | 1          | 57      | 47   |
| Ca$_8$(Si$_{15}$Li$_{10}$Al$_5$N$_{55}$) | Eu$^{2+}$ | 400                             | 645                             | 1 trigonal antiprismatic; 2 trigonal prismatic | 3          | 58      | 48   |
| Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$ | Eu$^{2+}$ | 460                             | 638                             | distorted octahedron       | 1          | 62      | 49   |
| Ba$_3$Li$_3$Si$_5$N$_{12}$ | Eu$^{2+}$ | 400                             | 515                             | Ba$_{1.4}$ distorted octahedron; Ba$_2$ quadratic prism; Ba$_3$ distorted tetrahedron | 4          | 84.7    | 51,52 |
| Ba$_3$Ga$_3$N$_3$      | Eu$^{2+}$ | UV                              | 638                             | Ba$_{1.4}$ distorted octahedron; Ba$_2$ quadratic prism; Ba$_3$ distorted tetrahedron | 4          | 84.7    | 51,52 |
| BaSi$_2$N$_2$O$_2$     | Eu$^{2+}$ | 380                             | 494                             | cuboid                     | 1          | 36      | 53–57 |
| β-SiAlON               | Eu$^{2+}$ | 400                             | 540                             | channel                    | -          | 55      | 58–64 |
| AlN                    | Eu$^{2+}$ | 290                             | 470                             | polyhedral (EuN$_{12}$)    | 2          | -       | 65–73 |
| α-Mg$_2$B$_2$N$_4$     | Eu$^{3+}$ | 340                             | 593 613                         | octahedral; distorted octahedra | 2          | sharp    | 75   |
| Li$_3$Si$_2$N$_2$      | Eu$^{3+}$ | 375                             | 550                             | polyhedra                  | 6          | sharp    | 76–77 |
| Li$_2$CaAl$_3$N$_2$    | Eu$^{3+}$ | 380                             | 615                             | polyhedra                  | 1          | sharp    | 78   |

β-SiAlON: Eu$^{2+}$. The equivalent substitution of Al—O and Si—N on the β-Si$_3$N$_4$ structure resulted in β-SiAlON.58 Controlled oxygen doping amount, $z$ as expressed in the general formula Si$_{3-z}$Al$_{2z}$O$_z$N$_{8-z}$ and with Eu$^{2+}$ as activator, a UV to blue light excitable green-emitting phosphor ($z = 0.0044$) was developed.59 Referred to as low-$z$, maintaining the amount of O low runs opposite from the Eu$^{2+}$ insolvility, including adverse changes in morphology.60 Although the observed emission revealed that Eu is somewhere in the structure, rare earth dopant mechanisms, whereby Si and C simultaneously dissolve. Herein, C atoms replaced N. Therefore, the evolution of the solid solution manifested through the c-axis compression with Si-condensed layer formation and the Eu-doped layer that further shrunk the $ab$ plane.61

The enhanced blue emission intensity with SiC is ascribed to Eu$^{2+}$ luminescence center in AlN emitting uniformly in the phosphor particle. The Eu$^{2+}$ is found in a Si single layer intercalated in the wurtzite AIN blocks, which consequently forms a Eu$_{12}$ cuboctahedron (Fig 17b),63 The addition of SiC, which yields the Al$_{12}$Si$_4$C$_4$N$_{16}$:Eu emission shifts the excitation spectra to the red region, thereby enhancing its eventual use in UV- to blue-light excitable LEDs. The emission peaks at 470 nm under 290 nm excitation (Figs. 17c, 17d). This narrow emission band is attributed to the generation of symmetric cubic cubo-octahedral coordination site forming (EuN$_{12}$)$_{12}$, which yields the Al$_{12}$Si$_4$C$_4$N$_{16}$:Eu$^{3+}$ emission.64

**Sharp line emission (f-f transition).**—α-Mg$_2$B$_2$N$_4$:Eu$^{3+}$. The rarity of Eu$^{3+}$ doped nitride phosphors made the nitridoborate α-Mg$_2$B$_2$N$_4$ an interesting system. The sharp emission lines resulted from the $f$-$f$ transition of Eu$^{3+}$ ions; however, these emission lines could

Figure 16. (a) The c-channel where Eu$^{2+}$ is accommodated in the β-SiAlON framework; (b) Excitation and emission profiles. Reprinted with permission from Ref. 58. Copyright 2017 American Chemical Society.
not be effectively excited by NUV-LED,\textsuperscript{75} thus restricting their use. In this cubic $\alpha$-$\text{M}_3\text{B}_2\text{N}_4$, two kinds of M sites are in a face-sharing arrangement and with the rigidity of the $[\text{N}=$-\text{B}=$\text{N}]_3=$ bond that generates a compact and stable lattice. The M’s are coordinated by six N atoms that form an octahedron in the center of the symmetry center, as well as a distorted octahedron (Fig.18a). Impurity resulting from the generation of vacancies could account for the shrinkage of the host lattice. When Eu$^{3+}$ replaces Sr or Ca and coordinates with N$^-$ in the host, the Eu$^{3+}$ 4f energy level allows the formation of luminescent centers in the bandgap. For Sr$_3\text{B}_2\text{N}_4$, the broad excitation band at around 340 nm encompasses the band-to-band transition. In addition, the Eu$^{3+}$ and N$^-$ charge transfer is possible because it extends to approximately 450 nm. However, Ca$_3\text{B}_2\text{N}_4$ involves approximately 300 nm for the band-to-band transition, and those for Eu$^{3+}$ the electrons transition are from 350 to 450 nm. These electrons emit sharp characteristic Eu$^{3+}$ lines that peak at 593 nm (Ca) and 613 nm (Sr) (Fig. 18b).\textsuperscript{75}

Li$_2\text{SiN}_2$: Eu$^{3+}$, Tb$^{3+}$. Through high-temperature solid-state reaction (900 °C, 1 h), using nitride starting materials. This orthorhombic structure features a super tetrahedron [Si$_4$N$_6$]N$_{4/2}$ and eight Li$^{+}$, which in turn comprises four SiN$_2$ tetrahedra. Six Li ion crystallographic sites are predominantly 6-N coordinated (two are tetrahedra and five N-coordinated). All these polyhedrals are distorted, thus rendering the Li sites to be skewed from the center of the symmetry. This phosphor features a broad excitation band that spans from 300 to 400 nm peaking at 357 nm, and the most intense among the sharp emission lines is at 612 nm. The broad excitation band does not encompass the absorption of the host but rather the Eu$^{3+}$-N$^{3-}$ charge transfer. Similarly, the Tb$^{3+}$ doped samples peak at 550 nm.\textsuperscript{76}

LiCaAlN$_2$: Eu$^{3+}$/Tb$^{3+}$. In a similar solid-state approach (900 °C, 3 h), the nitridoaluminate preparation affords sharp red and green line emissions with Eu$^{3+}$ and Tb$^{3+}$ as activators.\textsuperscript{77} This phosphor crystallizes into a monoclinic structure built upon bow-tie units of [Al$_2$N$_6$].\textsuperscript{78} Consequently, each bowtie links to another through edge-sharing. The phosphor possesses one Ca site which is 6-N coordinated. The host itself absorbs at 250–350 nm while the Eu$^{3+}$-doped sample extends the host from 350 to 420 nm. With 380 nm excitation, the strong red line emission has the most intense peak at 615 nm. Doping with Tb$^{3+}$ reveals a 4f $\rightarrow$ 5d transition at approximately 290 nm and a charge transfer band of approximately 343 nm. Also, the green emission peak is centered at 550 nm (Fig 19). By employing the Eu$^{3+}$-doped LiCaAlN$_2$ in a LED package, the device obtained a CCT of 6869 K and CRI of 75.3.\textsuperscript{77}

RE$^{3+}$-doped nitrides thus demonstrate the sharp line (narrow emission) but are practically not very interesting phosphor candidates for the existing LED design because of the weak f-f- absorption in the NUV, violet to blue spectral regions.

**Narrow-Band Emission**

By employing a red phosphor with narrow-band emission, p-LEDs can achieve the twofold target of high efficacy and lower cost to be a more competitive LED system.\textsuperscript{39} These finding are the motivation for the development of narrow-band emitting phosphors. Several crystallographic features can ensure narrow-band emission. The width of the emission band is expressed in cm$^{-1}$ or nm corresponding to the band width at half maximum (fwhm). Different structural and

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### Figure 17. (a) Formation of Eu layer in the AlN tetrahedral framework; (b) The tetrahedral (Al,Si)C,N$_4$ and the (C,N)$_{12}$ coordinated Eu site; (c) The change in the emission profile with increasing SiC; (d) The enhanced emission intensity with increased carbide content. Reprinted with permission from Ref. 68. Copyright 2015 American Chemical Society.
Figure 18. (a) Photoluminescence of α-M3B2N4 (M = Ca, Sr):Eu3+ after 370 and 340 nm excitation; (b) The distorted Ca2+, Eu3+, and regular Sr2+, Eu3+ octahedral site. Reprinted with permission from Ref. 75. Copyright 2017 American Chemical Society.

Electronic factors have been identified (Fig. 20) that accounts for this narrow emission bands.

Symmetry of activator sites.—The coordination site which the activator occupies is a key feature to the width of the emission band. The distance of the ligands has to be uniform in all directions to exert the same effect in all directions and ensure symmetric emission. This symmetry may lead to a small Stokes shift as demonstrated in other systems, whereby high activator symmetry enables small Stokes shift and consequently reduces the emission bandwidth.80 The cuboid coordination site is most akin to the equilibrium geometry of Eu2+. For example, octahedral geometry would have two axial bonds longer than the four equatorial bonds, as well as angular distortions that inevitably increase the structural relaxation with varying intensity in different directions in the excited state. This site redounds to the high vibrational levels, thereby more significantly contributing to the emission energy profile. This is expressed mathematically in the increase in S or the Huang-Rhys coupling factor. The increase in S leads to an increase in the Stokes shift.81,82

\[ E_{\text{stokes}} = (2S - 1)\hbar\omega, \]

The shapes of the absorption and emission spectra are explained by the coupling of electronic transitions to vibration. In a quantum mechanical perspective, the energy potential of the activator in the presence of its ligands results in vibrational states. The electronic transition of the emitting ion is a reflection of the change in the vibrational state thus giving rise to a set of electronic and vibrational transitions. This is manifested in fine structures that corresponds to vibronic transitions. The intensities represent the transition between the initial state and the final state, each which different vibrational quantum number, is described as the overlap of the vibrational wave-functions known as the Franck-Condon overlap factor. The energy maximum of the overlapped fine structures at increasing temperature depends on ΔQ, between the harmonic potential of the electronic ground and excited states as caused by the change in bonding due to change in electronic configuration. From quantum mechanical
Figure 19. (a) Photoluminescence excitation (615 nm) and emission of Li$_2$SiN$_2$:Tb$^{3+}$, and the diffuse reflectance spectra of the host, and doped phosphor; (b) Excitation band monitored at 545 nm, and emission after 343 nm excitation. Reprinted with permission from Ref.77. Copyright 2017 American Chemical Society.

Figure 20. Factors that contributes to narrow band emission.

Figure 21. Crystal structure of cuboid nitride phosphors.
site, though cuboid, is overcome by the disordering in the framework, thereby broadening the emission.

The cuboid coordination site becomes particularly interesting not as a unique and exclusive structural feature in nitride phosphors assuring narrow emission but because of the symmetry that it possesses. This symmetric coordination site is also observed in the trigonal antiprismatic site of Ca in Ca$_{18.75}$Li$_{10.5}$Al$_{39}$N$_{55}$. The presence of Eu in this site affords a narrow band of approximately 56 nm. The narrow coordination site of Ca in Ca$_{18.75}$Li$_{10.5}$Al$_{39}$N$_{55}$ also possess a symmetric coordination site albeit slightly distorted. The six N's are bonded, with two being the same and having the minimal spread, thus resulting in relative uniformity. Although the bond angles deviate from a perfect octahedral the effect of the ligands on the activator is well within small ranges. Other nitride that lack this symmetric coordination site are predisposed to have a broad emission. The distorted octahedral of the two Ca sites has nine interatomic distances that range from 2.31 Å to 2.74 Å. This wide spread of distances permits the differentiation caused by the chemical environment of the two sites, which leads to multiple emission bands in one site. The fwhm is 124 nm.

Homogeneity of activator coordination sites.—A single crystallographic activator site prompts the phosphor emission to be narrower than when two or more activator sites are present. This condition is particularly true for SrMg$_2$Si$_4$N$_4$, Sr$_2$LiAl$_4$N$_8$, and Li$_2$(Ca$_{1-x}$Sr$_x$)$_2$Mg$_2$Si$_2$N$_6$ because their narrow emission bands are attributed to the single cation crystallographic site. However, their narrow emission bands would have rendered the broad emission of SrLiAl$_4$N$_8$ because of the presence of two crystallographic sites. The two sites are very similar, and the ordered framework allows Eu$^{2+}$ to dope into Sr$_2$ site; thus, a narrow emission can be also observed in two possible sites. Similarly, the narrow red emission in Ca$_{18.75}$Li$_{10.5}$Al$_{39}$N$_{55}$ is from the trigonal prismatic site; although not cuboid, this site is a symmetric coordination site that conforms to the symmetric requirement. However, crystallographically, this Li,Al supertetrahedron has actually three Ca sites. The largest Ca-N distance of approximately 2.65 Å on Ca$_2$ sites is a logical basis to explain the emission due to the matching ionic radii of Eu$^{2+}$ and N$^-$ and the existing symmetry requirement. However, data suggest that the lowest absorption bands from the sixfold coordinated sites with the shortest Ca—N mean bond distance should be the emitting sites, namely Ca1 and Ca3 and are trigonal antiprismatic. Therefore, though more than two, the preferred occupancy to two but nearly similar sites introduced the narrow emission. Also, a case of uncontrolled O contamination exists, wherein the single crystallographic site of supposedly pure N coordination (EuN$_4$) generates Eu(N, O)$_x$ that effectively would have emission sites with distinct chemical environments; hence, a broad band emission is noted.

In the case of β-SiAlON, low z ensures a narrow emission band because the increase would result in the opposite. Owing to z which quantifies the amount of O in the system, an introduced inhomogeneity maintained low would lessen the possibility of energy transfer from the high 5d levels of the 5d of the Eu$^{2+}$ caused by variation in the crystal field around the Eu, among many possibilities.

Ordering and rigidity of the host lattice.—Apart from the striking cuboid feature and the number of sites, as well as the ordered packing, the degree of condensation, which pertains to the attributes of the host lattice, exerts influence in the generation of narrow emission bands. The Debye temperature is used as an indicator to express the degree of condensation, which pertains to the attributes of the host lattice and ensures a narrow emission band because the increase would result in the opposite. Owing to z which quantifies the amount of O in the system, an introduced inhomogeneity maintained low would lessen the possibility of energy transfer from the high 5d levels of the 5d of the Eu$^{2+}$ caused by variation in the crystal field around the Eu, among many possibilities.

Distance of activator sites.—The distance of one emission site to its nearest neighbor allows it to independently emit without the possibility of energy transfer as would be the case in high activator concentrations. The premise is that with same activator concentration, and in host lattices where dopants do not occupy discrete ion sites but rather are in channels as in the case of β-SiAlON. Here, the Eu$^{2+}$ do not actually substitute any of the ions in the lattice. Rather, it occupies the c- channels thereby acquiring the symmetric coordination environment. The distance of Eu$^{2+}$ in this channel is in the range of ~ 8 Å making energy transfer less probable. The distance of activators can be determined from the crystallographic data. Thus, distance would then be another criteria in establishing possible narrow band emission. This structural feature (rather than the usual concentration-based behavior) which causes energy transfer which can ensure narrow emission bands. It should however be taken with caution since minimal energy transfer leading to peak emission shift and broadening are usually ascribed to optimum activator concentration and unlikely to structural consideration.
Inherent emission of activators.—The search for narrow band emission with Eu³⁺ can also be circumvented by employing other activators. Coincidentally, the prevalence of mixed valence states of activators, especially Eu⁵⁺/Eu³⁺ in nitride phosphors, proves the stability of Eu³⁺ in some nitride hosts despite being subjected to a highly reducing atmosphere during sintering. The sharp emission lines of Eu³⁺ in the red region makes it particularly interesting as well (Fig. 22). The Ca and Sr variants of α-M₁³B₁₃N₄ are characterized by a broad excitation band at approximately 350–450 nm and the sharp emissions of Eu³⁺ at 593–735 nm with the most intense peak at approximately 613 nm.⁵¹ Also, a sharp emission is observed for 2 mol% Eu³⁺–doped LiSiN₂. After 357 nm excitation, emission peaking at 612 nm was also observed. Despite doping being in the non-symmetric Li site, Eu³⁺ inherently manifests its characteristic sharp emissions.⁷

Splitting of the highest f-level.—A quantitative descriptor is identified through the evaluation of electronic structures of known narrow- and broad-band emitting phosphors. A narrow band width can be achieved with a significant distance between the two topmost f bands. This narrow band width serves as a basis in the first principle screening of nitrides leading to the identification of five new nitride hosts with good chemical and thermal stability and desirable quantum efficiency.

The partial charge density for the highest 4f band of EuN₉ coordination is akin to a cuboid-like distribution similar to the 4fₓ₂,2 or 4fₓ₂₋₂,₂ orbitals. By contrast, the EuN₉ environment in β-SiAlON has partial charge density akin to a highly symmetric hexagonal distribution similar to 4fₓ₂,₂₋₂,₂, 4fₓ₂₋₂,₂, 4fₓ₂₋₂,₂, or 4fₓ₂₋₂,₂, with three lobes each aligned with the Eu—N bond, and the other three bisecting a pair of Eu—N bonds (Fig. 23a). This alignment and fitting does not appear to manifest in the lower f orbitals. The direct and close position of the f electron clouds with the position of the N ligands results in a high degree of electrostatic repulsion that renders these orbitals at high energies, consequently departing from orbitals that do not have direct electrostatic encounter with the ligands (Fig. 23b).⁸³

These models validate why hardly no existing trends can be derived from either host lattice rigidity or structural ordering of the lattice apart from the new set of cuboid phosphors and β-SiAlON, thereby serving as a direct and valid basis of narrow-band emission.

Thermal Stability

Thermal stability is one attribute of a phosphor that predicates the durability, longevity, and consistency of its performance in light-emitting devices in the desired working temperature at the very least, and ideally at even high temperatures. Phosphors could have very similar structures, but the conserved intensity of emission at an increasing temperature can be traced to its electronic structure. Thus, thermal stability is defined by the bandgap, chemical tunability, and the degree of condensation (Fig. 24).

The inverse relationship of emission intensity of the 5d–4f transition and temperature is given by:

\[ I(T) = I(0)/(1 + (\tau_0/\tau_e)\exp(-\Delta E/k_B T)) \]

where \( \tau_0 \) is the radiative decay rate corresponding to the state of the lanthanide, \( \tau_e \) is the attempt rate of the thermal quenching process, \( k_B \) is the Boltzmann’s constant, and \( \Delta E \) is the energy barrier for thermal quenching.⁸³

Various modalities wherein temperature quenches the luminescence of phosphors exist (Fig. 25). First, the autoionization model proposed by Dorenbos⁸⁴ found that the 5d orbital of Eu³⁺ is in close proximity with the CB of the host lattice before the crossing point of the 4f and 5d orbitals. This premise has also been deduced and validated from first principle calculations.⁸⁵ At a given temperature, the electron in the 5d orbital can be thermally activated, thereby enabling the transfer of electron to the CB. The electrons then dissipate its energy through non-radiative processes, such as occupying traps, defects acting as luminescence quenching centers, or in lattice vibrations. This finding suggests that the larger the gap between the 5d level to the CB, the more thermally-stable the phosphor.⁸⁴,⁸⁶,⁸⁷ The second mode is true cases where different valence states of activators coexist.⁸⁸,⁸⁹ This mode has been recently reported in Eu-doped SrLiAl₃N₄ and the Ce-doped green light-excitable SrMg₂Al₂N₄.⁹⁰ The third mode is based on the 4f–5d crossing model that is illustrated in configuration.
coordinate diagrams. The fourth mode is the transfer of electron holes from the ground state of the activator to the valence band (VB).

**Bandgap.**—Sufficient bandgap can ensure stability of the nitride phosphors and the presence of luminescence behavior. However, the distance of the 5d orbital of activator to the bottom of the CB more specifically describes its thermal stability.

One interesting example is SrLiAl₃N₄ and SrMg₂SiN₄, which have been investigated to compare their marked difference in thermal stability, despite the shared ordered Li, Al, and Mg-Si tetrahedra networks (Table II). Density of states (DOS) data reveal a remarkable level of covalency between the N ligands and Sr, which is expected to translate to the same behavior upon Eu doping. However, the band gaps of the two phosphors account for the observed difference in their thermal quenching temperatures.

SLA has 42% wider bandgap and more than twice the distance of the 5d orbital from the CB compared with SrMg₂SiN₄ (Fig. 26a). Therefore, the thermal quenching of phosphors is strongly affected by the amount of Eu, and the presence of defects may act as traps or as means toward non-luminescent relaxation. The origin of SrLiAl₃N₄ temperature stability being attributed to the δE is established; however, the cause of the marked difference in the distance of the 5d to the CB of SrLiAl₃N₄ and SrMg₂SiN₄ remains unclear.

The factors for this difference are the CFS and centroid shift, and these factors can be independently evaluated. Centroid shift is related to the polarizability of the anion, while N is dependent on its electronegativity. For SrLiAl₃N₄ and SrMg₂SiN₄, the Pauling electronegativities are nearly the same. The only factor that remains is the CFS. While CFS is generally influenced by coordination geometry, the coordination geometry in this case being both cubic implies that it is not a critical differentiating factor. The search shifts to the Eu—N distance which can account for the difference in bond length of the Eu—N forming the cuboid site. The smaller bond distance in SrLiAl₃N₄ results in a more red-shifted emission than SrMg₂SiN₄, suggesting that CFS is the most logical means to tune their luminescent characteristics. A shift toward low energy emissions (red-shift) could be obtained with a host lattice exerting strong crystal field. The desired improvement of thermal stability can be obtained by stabilizing the lower d levels at a considerably lower level from the CB. The stabilization of the Eu-5d orbitals is thus caused by centroid shift and NE.

Apart from SrMg₂SiN₄, the Ba variant which is known as BaMg₂SiN₄ reveals that it cannot be fitted in a single activation energy plot. However, these materials possess a few traps that are characterized with approximately 0.15 eV energy to liberate its trapped excitons, while the d→f transition is approximately 0.4 eV with a bandgap of approximately 4.0 eV. This bandgap is nearly identical with Sr and Ca, but thermally activated emission quenching is low in the Ba-doped sample. This finding means that the distance of the lowest 5d level is low from the bottom of the CB. The other U₇C₄C₄-type phosphors suffer from modest thermal stability, as in the case of MMg₂Al₂N₄. The BaMg₂Al₂N₄ thermal quenching fits a single activation energy with δE = 0.25 eV. This value is relatively close to SrLiAl₃N₄, but the Sr and Ca variants have more complex quenching behavior. The modest thermal stability challenges its full-swing development as phosphor materials for light-emitting diodes.

Apart from looking at the host lattice and the position of the emitting atom within the bandgap, optimizing the dopant concentration as in the case of CaAlSiN₃ is also crucial, where approximately 0.03 eV decrease is noted with 0.5% doping concentration. This result is attributed to the large splitting of the 5d orbitals and the observed decrease in the value of δE. As Eu increases, the Fermi level overlaps with the conduction band, thus, the bandgap vanishes. Here, the electrons can be automatically ionized from the excited state to the CB at high T. The location of the lowest 5d orbital in the excited state is a convenient determinant of thermal stability on nitride phosphors. In addition, the location predicts the probability of luminescent f-d transition among Lanthanide dopants, as well as the thermal stability of these nitride phosphor systems.

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**Table II. Structural and electronic properties of SLA and SMS.**

|                | Sr[LiAl₃N₄]⁴¹ | Sr[Mg₂SiN₄]⁴⁴ |
|----------------|----------------|----------------|
| crystal structure | Triclinic (P1, no. 2) | Tetragonal (I₄₁/a no.88) |
| tetrahedral arrangement | ordered | ordered |
| Eu—N bond distance, Å | 2.80 ± 0.10 | 2.86 ± 0.20 |
| ΔE (lowest d orbital→CB), eV | 0.28 | 0.13 |
| thermal property | excellent | poor |

**Substitutional variability toward solid solutions.**—The chemical tuning of phosphors entails the partial or complete editing of one or more elements in the host lattice or the cation or activator. This chemical substitution approach considers ionic size and charge compatibility with the parent phosphor, among others (Fig. 22b). Cation substitution is a prevalent strategy that conserves the crystal structure,
### Table III. Structural properties of narrow-band nitride phosphors.

| Phosphor | Host lattice elements | Anion | Unit structure | Ordering | Degree of condensation, $\kappa$ | Structural motif | Ref. |
|----------|-----------------------|-------|----------------|----------|----------------------------------|----------------|------|
| Sr[LiAl$_3$N$_4$] | Li, Al | N | tetrahedra, tetrahedra | ordered | 1 | edge- and corner-sharing | 41 |
| Ca[LiAl$_3$N$_4$] | Li, Al | N$^{[4]}$ | tetrahedra, tetrahedra | ordered | 1 | vertex- and corner-sharing | 42 |
| Ca[Mg$_2$Al$_2$N$_4$] | Mg, Al | N$^{[4]}$ | tetrahedra, tetrahedra | ordered | 1 | edge-sharing | 43 |
| Sr[Mg$_2$Al$_2$N$_4$] | Mg, Al | N$^{[4]}$ | tetrahedra, tetrahedra | ordered | 1 | edge-sharing | 43 |
| Ba[Mg$_2$Ga$_2$N$_4$] | Mg, Ga | N | tetrahedra, tetrahedra | ordered | 1 | edge-sharing | 43 |
| Sr[Si$_2$N$_2$O$_2$] | Mg, Si | N | tetrahedra, tetrahedra | ordered | 1 | corner-sharing | 44 |
| Sr$_4$[LiAl$_{11}$N$_{14}$] | Li, Al | N$^{[2]}$, N$^{[3]}$, N$^{[4]}$ | tetrahedra, tetrahedra | ordered | 0.71 | vertex sharing | 44 |
| Ba$_2$[Li$_2$(Al$_2$Si$_2$)N$_6$] | Li, Mg, Al, Si | N | tetrahedra, tetrahedra | ordered | 0.71 | corner- and edge-sharing | 44 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Si, Mg | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 45 |
| Sr$_2$[Li$_2$(Al$_2$Si$_2$)N$_6$] | Li, Al, Si | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 45 |
| Ba$_2$[Li$_4$Si$_7$Al$_2$N$_12$] | Ga | N | tetrahedra, tetrahedra | ordered | - | - | 46 |
| Sr$_2$[Li$_2$(Al$_2$Si$_2$)N$_6$] | Li, Mg, Al, Si | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 47 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Li, Mg, Al, Si | N | tetrahedra, tetrahedra | ordered | - | - | 48 |
| Ca$_{18.75}$Li$_{10.5}$Al$_{39}$N$_{55}$ | N$^{[2]}$, N$^{[3]}$, N$^{[4]}$ | tetrahedra, tetrahedra | ordered | 0.71 | vertex sharing | 49 |
| Ba$_2$[Li$_2$(Al$_2$Si$_2$)N$_6$] | Si, Mg | N | tetrahedra, tetrahedra | ordered | - | - | 50 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Li, Al, Si | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 50 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Li, Al, Si | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 50 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Li, Al, Si | N | tetrahedra, tetrahedra | ordered | 0.6 | edge-and corner sharing | 50 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Li, Al, Si | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 51–57 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Li, Al, Si | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 58–64 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Li, Al, Si | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 65–73 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Li, Al, Si | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 74–77 |
| Sr$_2$[Li$_2$Ca$_2$Mg$_2$Si$_2$N$_6$] | Li, Al, Si | N | tetrahedra, tetrahedra | ordered | - | edge-sharing | 74–77 |

which could also lead to the transformation of the parent phosphor into a totally new structure.41,42,44,45

The introduction of Ca in $(\text{Sr}_{1-x}\text{Ca}_x)\text{LiAl}_3\text{N}_4$ improves the crystallinity and the photoluminescence of the parent phosphor. Though consistently red-shifted further with the addition of Ca, the intensity peaks at approximately $x = 0.2$. The asymmetric although still narrow peak can be accounted to the doping of the two Sr sites, though results suggest preferential occupancy of the Sr2 site with ionic radii considerations as the driving force.101 This substitution also redounds to increased activation energy according to the configuration coordinate diagram.102

In tuning the host lattice, solid solutions are formed. In addition, these solutions are gateways not only in developing new phosphors but also in gaining insight to the mechanism of structural evolution, which manifests some interesting luminescence and thermal behavior.

Interestingly, SrMg$_2$Si$_2$N$_4$ and SrLiAl$_3$N$_4$ are the extreme ends of the solid solution; by substituting Li$^+$ to Si$^{4+}$ and Al$^{3+}$ to Mg$^{2+}$, charges remain balanced in the given chemical formula. The stabilization of SrMg$_2$Si$_2$N$_4$ from the introduction of Li$^+$ and 3Al$^{3+}$ are expected to replace the small isoelectronic 3Mg$^{2+}$ and Si$^{4+}$ which can enable the former to achieve the desirable properties of the latter. The extreme end of this solid solution is ultimately generating SrLiAl$_3$N$_4$, which has the desired thermally stable narrow red emission, albeit too red shifted.

## Spectral Diversification

Spectral diversification refers to a multitude of strategies to tailor the properties of these narrow-band phosphors to respond to the evolving needs and requirements of its application (Fig. 27). The various synthetic strategies such as employing flux, post treatment, and coating offer solutions to compromise the properties of these phosphors.105

Computational approaches and/or experiments have led to better understanding of the structural, electronic, optical, and thermal properties of a wide range of nitrides, gaining insight and control over its continuous discovery and development. The much desired narrow emission and thermal stability thus become the yardstick for the

![Figure 26. (a) Band structure illustrating the thermal energy difference of the d-orbitals of SrMg$_2$Si$_2$N$_4$ and SrLiAl$_3$N$_4$ with respect to the CB; (b) Solid solution of SLA and SMS.](image)

![Figure 27. Strategies toward spectral diversification of nitride phosphors.](image)
screening and investigation of new phosphor candidates. The classes of phosphors allude its novelty and patentability, being equally significant especially in catering to the existing and emerging needs of the industry.\textsuperscript{107} Several strategies may be offered toward the discovery and design of new types of phosphors based on existing or from entirely new hosts.\textsuperscript{108} Of these classes, un-doped hosts and entirely newly discovered structures present novelty and economic opportunity.

The narrow band emission particularly becomes relevant in LED in the red region where IR spill over must be reduced. The presence of a red component that is not too red-shifted has been demonstrated in Ce-doped nitride. Although deviating from the narrow-band emission, several other options still remain. Cerium has been doped on other nitrides and has revealed interesting photoluminescence as shown in Figure 28.\textsuperscript{109–112} In the case of SrMg\textsubscript{2}Al\textsubscript{2}N\textsubscript{4}, the excitation profile is a broad one at 520 nm (green); hence, the term green-light excitable. The excitation profile is a broad two-peaked emission albeit over-lapped with a maximum at 580 and 620 nm. This phosphor has been used to generate white light in a new configuration in LED assembly, lapped with a maximum at 580 and 620 nm. This phosphor has been discovered structures present novelty and economic opportunity.

Solid solution strategy.—Solid solutions have been developed to modify and improve photoluminescence and thermal properties of nitride phosphors.\textsuperscript{4,114–116} Partially (or completely) substituting the cation would have significant effects on the CFS, especially in cases where the structure remains the same as in the case of M[LiAl\textsubscript{2}N\textsubscript{4}] (M = Ca, Sr, Ba) and M[LiAl\textsubscript{2}N\textsubscript{4}] (M = Ca, Sr) or when it changes as in the case of M[Mg\textsubscript{3}SiN\textsubscript{4}] (M = Ca, Sr) from the Ba variant. This finding redounds to changes in emission peak position and even thermal properties. Apart from the cation, the anion framework could also be modified. The isoelectronic M[Mg\textsubscript{3}SiN\textsubscript{4}] could be substituted with Al for Mg and Li for Si while the change balance is conserved. The extreme end of this is M[LiAl\textsubscript{2}N\textsubscript{4}]. This end could provide means to improve the inferior properties of M[Mg\textsubscript{3}SiN\textsubscript{4}]. The anionic framework of M[Mg\textsubscript{2}Al\textsubscript{2}N\textsubscript{4}] could be partially substituted 2Si\textsuperscript{4+} + M\textsuperscript{2+} = 2Mg\textsuperscript{2+} + 2Al\textsuperscript{3+} while the cation M can be substituted with 2Li\textsuperscript{+} or any other M\textsuperscript{2+}. A possible structural result could be Li\textsubscript{2}Mg\textsubscript{4}Si\textsubscript{3}N\textsubscript{6} (M = Ca, Sr), which has structurally been partially mentioned in reports\textsuperscript{41} but has not been thoroughly discussed or reported.

Narrow-band nitride phosphors as in the case of Li\textsubscript{2}Ca\textsubscript{3}[Mg\textsubscript{3}Si\textsubscript{2}N\textsubscript{6}]:Eu\textsuperscript{2+} have successfully demonstrated that substituting Ca with the large Sr ion conserved a pure phase up to 0.07 mol% substitution. This conservation resulted in a 4 nm blueshift from the original 638 nm peak emission.\textsuperscript{49} The narrow-green phosphor Ba[Li\textsubscript{2}(Al\textsubscript{2}Si\textsubscript{2})N\textsubscript{6}]:Eu\textsuperscript{2+} peaks at 532 nm. The introduction on Mg that replaces Li resulted in a redshift to approximately 560 nm (mol% Mg = 0.1) and 562 nm (mol% Mg = 0.2). This substitution allows the introduction of Mg and more Al (lesser Si), wherein the Al\textsuperscript{3+} has lower inductive effect compared to Si\textsuperscript{4+} and a low Al\textsuperscript{3+} ratio increased the NE; thus, the observed shift has long wavelengths.\textsuperscript{47}

Unexplored, new, and un-doped nitrides.—Several approaches may lead to new phosphor materials as outlined in Figure 29. An old phosphor that has not been used for LED and solid solutions of known phosphors, as mentioned in 5.2 could provide new phosphors albeit with the inherent challenge to navigate through patents to establish novelty. The two other remaining classes have secured the novelty component which is crucial in protecting such with a patent. A completely new material that would need to hurdle the arduous task of determining the right structure is undeniably an effective strategy. However, materials which might be known, but have not been doped or used as phosphor, would also be equally promising.\textsuperscript{117}

Several undoped and promising new nitride hosts fuel research and development toward exciting new phosphors and in gaining insights

Figure 28. Excitation and emission profile of Ce-doped nitride phosphor hosts. (a) SrMg\textsubscript{2}Al\textsubscript{2}N\textsubscript{4}\textsuperscript{90} (b) SrMg\textsubscript{3}SiN\textsubscript{4}\textsuperscript{44} (c) Li\textsubscript{2}(Ca\textsubscript{1-x}Sr\textsubscript{x})[Mg\textsubscript{2}Si\textsubscript{2}N\textsubscript{6}].\textsuperscript{49} Reprinted with permission from References 90, 44, 49. Copyright 2016, 2014, 2017. American Chemical Society.
| Host                  | # of cation site/s | Shape of cation site                  | Structural motif                      | Ordering        | Space Group | Ref. |
|----------------------|--------------------|---------------------------------------|---------------------------------------|-----------------|-------------|------|
| Ca$_2$Ga$_3$MgN$_5$  | 1                  | distorted capped octahedron (CaN$_7$) | edge- and corner-sharing tetrahedra (Ga,Mg)N$_4$ | disordered      | C2/m (no. 12) | 118  |
| Ca$_3$Mg$_5$GeN$_6$  | 1                  | octahedron (CaN$_6$)                  | corner-sharing tetrahedra and trigonal planar (Mg,Ge)N$_4$ | disordered      | P6$_3$/mmc (no. 194) | 119  |
| CaMg$_2$GaN$_3$      | 1                  | octahedron (CaN$_6$)                  | corner-sharing of trigonal planar Mg,Ga w/ N | disordered      | P6$_3$/mmc (no. 194) | 120  |
| CaMg$_2$Ga$_3$N$_4$  | 1                  | octahedron (CaN$_6$)                  | edge- and corner-sharing (Mg,Ga)N$_4$ | disordered      | P3$_m$1 (no. 164) | 121  |
| Ca$_4$Mg$_3$Ge$_3$N$_{10}$ | 1      | polyhedron (CaN$_7$)                  | edge- and corner-sharing (Mg,Ge)N$_4$ | disordered      | C2/m (no. 12) | 122  |
| Sr$_2$Mg$_3$Ga$_4$N$_{13}$ | 1      | polyhedron (CaN$_7$)                  | Mixed (Mg,Ga)N$_4$ tetrahedra and trigonal (Mg,Ga)N$_3$ | disordered      | C2/m (no. 12) | 123  |
| Ca$_2$Mg$_2$Ga$_3$N$_5$ | 1      | octahedron (CaN$_6$)                  | edge-sharing (Ga,Mg)N$_4$ | disordered      | P6$_3$/mmc (no. 194) | 124  |
| Ca$_2$Mg$_2$Ga$_2$N$_4$ | 1      | octahedron (CaN$_6$)                  | edge- and corner-sharing (Ga,Mg)N$_4$ | disordered      | P$_6_3$/m (no. 164) | 125  |
| B$_3$Ga$_2$N$_4$     | 2                  | polyhedron (CaN$_7$)                  | edge-sharing GaN$_4$ | -               | Pnna (no. 52) | 126  |
| Sr$_3$Ga$_2$N$_4$    | 2                  | polyhedron (CaN$_7$)                  | trans-edge-sharing GaN$_4$ | -               | Pnna (no. 52) | 127  |
| Ca$_3$Ga$_2$N$_6$    | 2                  | octahedron (CaN$_6$)                  | edge- and corner-sharing GaN$_4$ | -               | C2/c (no. 15) | 128  |
| Li$_2$M$_2$Si$_2$N$_4$ (M = Ca, Sr) | 2      | trigonal (anti) prism; polyhedron | corner-sharing | -               | Pn3 | 129  |
| Li$_2$Ca$_2$Si$_2$N$_5$ | Li-2 | Ca-3 | distorted octahedron (CaN$_6$) | edge- and corner sharing | Pnma (no. 62) | 130  |
| Sr$_3$Ga$_2$N$_5$    | 3                  | octahedron (CaN$_6$)                  | trans-edge- and corner-sharing GaN$_4$ | -               | P1 (no. 2) | 131  |
| Li$_2$Sr$_3$Ga$_2$N$_2$ | Sr-3 | Li-2 | Sr- distorted octahedron Li-distorted tetrahedron | corner and edge -sharing GaN$_4$ | -               | C2/m (no. 12) | 132  |
| Sr$_3$Ti$_7$N$_{10}$ | 1                  | polyhedron (SrN$_{13}$) | corner and edge -sharing Si$_4$ | -               | Pnca (no. 51) | 133  |
| Ca$_3$RE$_3$Si$_9$N$_{17}$ (RE = Sm, Yb) | 2      | cuboid (CaN$_6$) | supertetrahedrone- | -               | P4$_3$m | 134  |

on the performance of nitride phosphors. Some of these performances are outlined in Table IV.

**Outlook**

The evolving consumption and lifestyle establishes the improvement in various industries. In pc-LED, existing and emerging opportunities are not only in R&D but also in actual industrial cross over that sustains the interest phosphors. Figure 30 shows the opportunities in lighting, biomedical, design and display, agriculture, and communication. In the future, the existing uses and emerging frontiers justify the resources utilized toward the continuous.

*LED lighting.*—The quest for improved LED performance and the emergence of new frontier to foray serves as a driving forces behind the continuous discovery, research and development, and commercialization of phosphors in general.

The target discovery and improvement toward narrow-band phosphors based on a spectral model of pc-LED with red and green phosphors directs the optimization of CE as predicated by bandwidths and peak positions (Fig. 31). The CE refers to the lm/W rating. The high CRI due to the use of a red phosphor and the cheap system cost are already the advantages of pc-LED, further enhancing its efficacy without unduly compromising its secured edge. Thus, the quest for...
narrow band reds that are thermally stable peaks at around 620 nm and have high intensity among others still challenges phosphor R&D.

Given the advantage of pc-LEDs, it is most likely to maintain the lead if not render obsolete conventional and energy inefficient lighting technologies. However, the disturbing issue against blue LED regarding altering flora and fauna circadian clocks constitute what would yet become a major setback. The tunability of phosphors and the presence of a wide variety of choices, particularly those that could be excited by violet or UV light, offers a potential solution to circumvent this stumbling block. Redesigning the LED package would consequently follow in response to this issue. The controllability of the components, fabrication, and use of LED and its relative energy efficiency\textsuperscript{134} catapults it in yet an interesting ride toward extensive and significant use in the future. More than the exciting LED virtual sky panels, wall paper to contact lens, and even eyelashes,\textsuperscript{132} the promise of diversified and levelled-up requirement for LED is rising. Amidst the still consistent market base for troffers, LED panel light, tunnel and highway light, and wall washers, the burgeoning smart lighting and communication applications are emerging.\textsuperscript{133}

Once rendered in nano range sizes where these phosphors are not subject to quantum size effects, narrow band phosphors will also be relevant in microLED lighting and display applications which is gaining momentum toward full swing commercialization.

\textbf{Agriculture lighting.---}In view of their emission in the red spectral region, the opportunity that nitride phosphors offer is in food agriculture, either employed in light conversion films (LCF) or as LED plant lamp (LED-pl).\textsuperscript{134} Enhancing the actual 1\% utilization of sunlight by plants through photosynthesis would mean enhanced crop yield and productivity.\textsuperscript{135} The spectral specifications include emission at 400–470 nm (blue) and 600–680 nm (red) for LED-pl (Fig. 32), which corresponds to the range of useful wavelength for plants. For LCF, phosphor that may be UV-light (280–380 nm) and green-light excitable property of SrMg\textsubscript{2}Al\textsubscript{2}N\textsubscript{4} and even SrLiAl\textsubscript{3}N\textsubscript{4} creates new avenues toward the development of new phosphor systems for light converting films. The stability, ease of processing, and durability of the film are part of the key features that warrant further investigation to design the materials for prolonged solar irradiation and exposure to elements, such as heat and humidity. The use of LED in plant cultivation has been demonstrated by NASA in the 1960’s\textsuperscript{137} and has not gone through rigorous development since. The full automation of plant cultivation makes LED lighting compatible because it can be remotely managed. With the increasing food and energy requirements, LED technology will certainly respond to ensure food security.\textsuperscript{133}

Developments in this field not only consider short-term benefits as improved harvest or circumvented seasonality of crop production but also in ensuring food sufficiency for a growing population.

\textbf{Persistent luminescence.---}Persistent luminescent materials have extensive and practical applications in markings and signage, display and aesthetics, textile printing and design, and biomedical applications.\textsuperscript{138–142} The need to improve brightness and decay time paved the way for long emission with appropriate brightness to cater to the evolving practical applications, thereby\textsuperscript{143} catapulting the development of persistent phosphors to the fore. Persistent luminescence is a phenomenon wherein a temperature-dependent material continuously emit light in the visible spectral range in the order of seconds to several hours after the excitation has ceased.\textsuperscript{144,145}

Figure 33 demonstrates through the Dorenbos model how electrons from the 4f level are excited to the 5d level. The inherent proximity of the 5d to the CB enables the electrons to move to a trap. These traps can be structural defects or other chemical species (such as Tm, Dy, and Sm) that are capable of accepting the electron by heat, which can release the electron back to the CB. Thus, a radiative emission exists over a long period of time without the excitation source. Filling the red gap in the color spectrum of persistent luminescence materials fits the emission wavelength range of most nitride phosphors. The emission intensity, as well as the presence of red-emitting material, suffices the human eye sensitivity to red especially for low-light conditions.\textsuperscript{146,147}

A limited number of red nitride phosphors have been developed, belonging to the MSi\textsubscript{2}N\textsubscript{6} (M = Ca, Sr, Ba) family as summarized in Table V.\textsuperscript{148–156} The presence of inherent defects, as well as the
introduction of additional defects acting as traps, such as co-dopants (Tm, Dy, Nd, and Sm) in multiple overlapping states, compliment the ability to induce persistent luminescence in thermally compromised phosphor systems. A low quenching temperature would render the lowest 5d state in a very close proximity with the CB facilitating charge trapping under blue-light excitation. Apart from SrLiAl3N4, all the other cuboid nitride phosphors have compromised thermal stabilities, thereby making them promising candidates for persistent luminescent phosphors. The reported presence of trapped excitons in SrMg2Al2N4 and BaMg3SiN4 predispose the potential of these systems even without the addition of co-dopants acting as traps.

Red persistent luminescence is rare, and nitride phosphors offer a wide array of systems for persistent luminescent applications. Apart from the exciting applications, comprehending the mechanism of this phenomenon would mean gaining control over the discovery, design, and development of more persistent luminescent phosphor.

Communication and data delivery.—Visible light communication (VCL) and Li-Fi are emerging in communication technology. Similar to a signal lantern, data transmitted through a power line is linked to a signal lantern, thereby proving that long wavelength light of approximately 525 nm does have potency apart from UV and blue LED.164 The red LED showed that it has adverse effect on three common pathogenic bacteria, thereby proving that long wavelength light of approximately 525 nm does have potency apart from quartz tungsten halogen light effectively thus, inhibiting human gingival fibroblast cellular proliferation.160 Similarly, in another dental application, a 630 nm LED light was also proven as an effective inhibitor, thereby making it a promising anti-inflammatory induction technique.159 Blue LEDs can also generate ROS more effectively than quartz tungsten halogen light effectively thus, inhibiting human gingival fibroblast cellular proliferation.160 Similarly, in another dental application, a 630 nm LED light was also proven as an effective inhibitor, thereby making it a promising anti-inflammatory 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