Facile Atmospheric Pressure Synthesis of High Thermal Stability and Narrow-Band Red-Emitting SrLiAl3N4:Eu2+ Phosphor for High Color Rendering Index White Light-Emitting Diodes

Xuejie Zhang,† Yi-Ting Tsai,† Shin-Mou Wu,‡ Yin-Chih Lin,§ Jyh-Fu Lee,§ Hwo-Shuenn Sheu,§ Bing-Ming Cheng,§ and Ru-Shi Liu*†,⊥

†Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
‡National Chung-Shan Institute Science & Technology, Chemical Systems Research Division, Taoyuan 325, Taiwan
§National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan
⊥Department of Mechanical Engineering and Graduate Institute of Manufacturing Technology, National Taipei University of Technology, Taipei 106, Taiwan

Supporting Information

ABSTRACT: Red phosphors (e.g., SrLiAl3N4:Eu2+) with high thermal stability and narrow-band properties are urgently explored to meet the next-generation high-power white light-emitting diodes (LEDs). However, to date, synthesis of such phosphors remains an arduous task. Herein, we report, for the first time, a facile method to synthesize SrLiAl3N4:Eu2+ through Sr3N2, Li3N, Al, and EuN under atmospheric pressure. The as-synthesized narrow-band red-emitting phosphor exhibits excellent thermal stability, including small chromaticity shift and low thermal quenching. Intriguingly, the title phosphor shows an anomalous increase in theoretical lumen equivalent with the increase of temperature as a result of blue shift and band broadening of the emission band, which is crucial for high-power white LEDs. Utilizing the title phosphor, commercial YAG:Ce3+, and InGaN-based blue LED chip, a proof-of-concept warm white LEDs with a color rendering index (CRI) of 91.1 and R9 = 68 is achieved. Therefore, our results highlight that this method, which is based on atmospheric pressure synthesis, may open a new means to explore narrow-band-emitting nitride phosphor. In addition, the underlying requirements to design Eu2+-doped narrow-band-emitting phosphors were also summarized.

KEYWORDS: narrow-band-emitting, high-CRI, white LEDs, red nitride phosphor, high thermal stability

1. INTRODUCTION

Currently, producing an efficient illumination-grade white light with a suitable correlated color temperature (CCT: 2700–4000 K), a conspicuous color rendering index (CRI > 85) with optimized luminous efficacy (LE) remains an outstanding challenge in the field of lighting.1−3 In today’s omnipresent light sources, most commercially available phosphor-converted white light-emitting diodes (LEDs) are based on a broadband YAG:Ce3+ yellow phosphor and an InGaN-based blue-emitting LED chip. This type of white LEDs can provide a high conversion efficiency, close to the theoretical maximum. However, the absence of red light in the emission spectral region of the light source resulted in a cool-white (high CCT) with a low CRI. To attain high-quality white light (CRI > 85), nitride phosphors, such as (Ba,Sr)2Si5N8:Eu2+,1 CaLiAl3N4:Eu2+,10 SrMg2Al13N20:Eu2+,11 SrMg3AlN4:Eu2+,12 and Ca18.75Li10.5Al39N55:Eu2+,13 some of these phosphors exhibit poor luminescence efficiency, whereas some are exceedingly red. Meanwhile, several of these phosphors show a disorder structure and more than one crystallographic site. To date, a narrow-band red-emitting phosphor SrLiAl3N4:Eu2+, with an emission band, and a significant part of light beyond 650 nm is located outside the sensitivity curve of the human eye, causing great loss in LE.4−9 To further improve the LE while maintaining CRI, a narrow-band (full width at half-maximum (fwhm) ≤ 60 nm) red-emitting phosphor with appropriate peak position (~630 nm) is urgently needed.

Recently, Schnick and colleagues reported several narrow-band red-emitting phosphors, with representative phosphors including SrLiAl13N4:Eu2+,1 CaLiAl13N4:Eu2+,10 SrMg2Al13N20:Eu2+,11 SrMg3AlN4:Eu2+,12 and Ca18.75Li10.5Al39N55:Eu2+.13 Some of these phosphors exhibit poor luminescence efficiency, whereas some are exceedingly red. Meanwhile, several of these phosphors show a disorder structure and more than one crystallographic site. To date, a narrow-band red-emitting phosphor SrLiAl3N4:Eu2+, with an

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emission peak position at ~650 nm and an fwhm of ~50 nm, was regarded as the most promising red phosphor for use in next-generation lighting because of the material’s excellent luminescent properties of low thermal quenching and high external quantum efficiency (QE). SrLiAl$_3$N$_4$ possesses an extraordinary structure (Figure 1b) as follows: (1) highly rigid framework of edge- and corner-sharing AlN$_4$ and LiN$_4$ tetrahedral with a degree of condensation $k$ (i.e., atomic ratio of (Li:Al):N) in this compound up to unity; (2) ordered distribution of LiN$_4$ and ALN$_4$ tetrahedral; and (3) cuboid-like SrN$_4$ and the activator Eu$^{2+}$ (1.25 Å) with almost the same size as Sr$^{2+}$ (1.26 Å). All these structural contributions contribute to the high performance of the SrLiAl$_3$N$_4$:Eu$^{2+}$ red phosphor. Therefore, SrLiAl$_3$N$_4$:Eu$^{2+}$ may be commercialized in the future for the fabrication of next-generation high-CRI white LEDs.

The reported synthesis method of SrLiAl$_3$N$_4$:Eu$^{2+}$ in literature is complex, and the raw materials are not readily available, hence limiting the further study and actual application of the red phosphor. In this paper, we report a facile synthesis method using SrN$_2$, Li$_2$N, metal powder of Al, and EuN as the raw materials under atmospheric pressure. The structure, morphology, luminescent properties including vacuum ultraviolet (VUV) spectrum, lifetimes, the valence state of Eu, thermal quenching behavior, and chromaticity stability of the title SrLiAl$_3$N$_4$:Eu$^{2+}$ phosphor are studied in detail. A warm white LEDs with CRI of 91.1 ($R_9 = 68$) and CCT = 2875 K was fabricated by employing red phosphor SrLiAl$_3$N$_4$:Eu$^{2+}$, commercial yellow phosphor YAG:Ce$^{3+}$, and blue LED chip.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. The narrow-band red-emitting phosphor SrLiAl$_3$N$_4$:Eu$^{2+}$ with 2.0 mol % Eu activator was made using solid-state reaction methods. The raw materials were Sr$_2$N$_2$ (Materion, 99.5%), Li$_2$N (Alfa Assaad, 99.9%), Al (Showa, 99.9%), and EuN (Cerac, 99.9%). The elemental precursors were weighed and ground using an agate mortar and pestle in an argon-filled glovebox (H$_2$O < 1 ppm, O$_2$ < 1 ppm). Then, the mixture was transferred into molybdenum crucibles and sintered at 1000 °C for 4 h under a 90% N$_2$–10% H$_2$ gas mixture in a tube furnace. The product was slowly cooled to room temperature inside the tube furnace under N$_2$–H$_2$ flow and was then ground to powder for further characterization. Commercial CaAlSiNi$_2$:Eu$^{2+}$ red-emitting phosphor was used as a reference to compare chromaticity stability as a function of temperature.

2.2. Characterization. Sample structure information was measured by Synchrotron X-ray diffraction pattern (SXRD; $\lambda = 0.4959$ Å) using the BL01C2 beamline at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The crystal structure was refined by TOPAS 4.2 software. The powder X-ray diffraction (XRD) pattern was also studied by Bruker D2 with Cu Kα radiation ($\lambda = 1.5405$ Å) at 30 kV and 30 mA. Optical properties of the excitation and emission spectra were obtained by Edinburgh FP920 combined fluorescence lifetime and steady-state spectrometer with a 450 W xenon lamp and thermodiode cooled red sensitive photomultiplier tube. The luminescence decay curves were measured by Edinburgh FP920 using a 150 W n9000 ns flash lamp with a pulse width of 1 ns and pulse repetition rate of 40 kHz as the excitation source. The temperature-dependent emission spectra were recorded on a Fluoromax-3 spectro-photometer setup with a 150 W Xe lamp and Hamamatsu R928 photomultiplier tube using a THMS-600 heating equipment. The vacuum ultraviolet (VUV) photoluminescence emission (PL) and excitation (PLE) spectra was obtained using the BL03A beamline at the NSRRC, Taiwan. The PLE spectra were recorded by scanning a 6 m cylindrical grating monochromator with a grating of 450 grooves/mm, which spanned the wavelength range of 100–350 nm. A LiF plate served as a filter to remove the high-order light from the synchrotron. The emission from the phosphor was analyzed with a 0.32 m monochromator and was detected with a photomultiplier (Hamamatsu R943–02) in a photon-counting mode. For measurements of low-temperature spectra, the sample holder was attached to a cryo-head of a helium closed-cycle cryostat system (APD HC–DE204S), which was mounted on a rotatable flange so that the sample could be rotated to $\sim 45^\circ$ with respect to both the incident VUV source and the entrance slit of the dispersed monochromator. The temperature control unit provided the cold head of the cryostat to be kept at $\pm 1$ K during the data collection period. The $\lambda$-edge of Eu was observed by X-ray absorption near-edge structure on transmission mode at BL17C beamline (NSRRC, Taiwan). Incident beam intensity ($I_0$) was measured by gas-ionization chambers filled with He and N$_2$ gases, whereas transmitted beam intensity ($I$) was measured using Ar and N$_2$ gases. The particle size and morphology of the sample were measured using scanning electron microscopy (SEM, Nova NanoSEM 450, FEL, Oregon, USA), and the elemental composition was determined using an energy-dispersive X-ray spectroscopy (EDX) that was attached to the SEM. The electroluminescence was recorded using a spectro-photometer with integrated spheres (EVERFINE, PMS-80) at 20 mA forward current. $^3$Al solid-state magic-angle spinning (MAS) NMR and $^7$Li solid-state MAS NMR spectra were acquired on a wide-bore 14.1 T Bruker Avance III NMR spectrometer, equipped with a 1.9 mm and 3.2 mm double-resonance MAS probehead for Al and Li, respectively. The Larmor frequency for $^7$Li was 233.3 MHz. The samples were spun at 35 kHz. A selective $\pi/4$ pulse of 0.8 μs for Al and $\pi/6$ pulse of 1.7 μs for Li were used for central-transition excitation. The recycle delays were 1 s for Al and 2 s for Li. The chemical shift was referenced to 1 M Al(NO$_3$)$_3$ aqueous solution.
3. RESULTS AND DISCUSSION

The powder X-ray diffraction (XRD) pattern of SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) is shown in Figure S1. Such pattern is highly consistent with the reported pattern of SrLiAl\(_3\)N\(_4\) except for some weak diffraction peaks from the second-phase AlN. To confirm the structure and evaluate the content of impurity, we performed Rietveld structure refinement for SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) using the powder synchrotron X-ray diffraction (SXRD) data through the TOPAS 4.2 software. The initial parameters were obtained from the single-crystal SrLiAl\(_3\)N\(_4\) reported by Schnick’s group.\(^1\) The experimental, calculated, and difference Rietveld refinement XRD patterns at room temperature are shown in Figure 1a, and the main parameters from the processing and refinement of the data are presented in Table S1. Almost all the diffraction peaks can be indexed to the corresponding data and gave a goodness-of-fit parameters of \(R_{wp} = 3.65\%\), \(R_{B} = 2.36\%\), and \(\chi^2 = 1.08\). The second-phase AlN was quantified to be \(\sim 5.48\) wt % from Rietveld refinement.

The as-synthesized phosphor shows a pink colored powder in Figure 2a; the powder gave an intense red light under 254 nm lamp irradiation. The excitation and emission spectra of SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) at 298 K are depicted in Figure 2c. SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) shows a peak at 650 nm with an fwhm of 55 nm (1279 cm\(^{-1}\)) under 460 nm excitation. The CIE chromaticity coordinates of SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) were determined to be \((0.705, 0.295)\), which was close to the chromaticity coordinates \((0.713, 0.286)\) was chosen as a reference. Using the equation of reference (equation from Supporting Information),\(^2\) the color purities of SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) and CaAlSiN\(_3\):Eu\(^{2+}\) were determined to be 98% and 87%. The result indicates that SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) exhibits a higher color purity compared with commercial red phosphor. The excitation spectrum (\(\lambda_{ex} = 650\) nm) includes two parts: the former is the VUV spectral range, and the latter is ultraviolet—blue—green—red spectral range. According to diffusion reflection spectrum of SrLiAl\(_3\)N\(_4\), the high-energy absorption bands (below 375 nm) are mainly ascribed to the absorption of the host lattice, and the low-energy absorption band was assigned to the allowed electronic transition from \(4f^7(8S_7/2)\) to \(4f^6(7F_J)5d^1\) (\(J = 0\,–\,6\)) within Eu\(^{2+}\).

The robust absorption band from 400 to 600 nm indicates that this phosphor can be effectively excited by blue LED. The crystalline morphology of SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) was checked by scanning electron microscopy (SEM) and is shown in Figure 2e. The observed particle size was below 5 \(\mu\)m. The atomic ratios Sr/Al/N of 1:3.08(2):4.45(6) determined by energy-dispersive X-ray (EDX) are in good accordance with the formula SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\). However, a slight overestimation of nitrogen was observed, and Eu was not detected under SEM/EDX as a result of lower dopant content. To further verify the incorporation of Li, we performed \(^7\)Li solid-state MAS nuclear magnetic resonance of SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) (Figure 2b). One sharp isotropic signal with chemical shift value of \(\delta = 2.55\) ppm was observed in Figure 2b, similar to that reported in the reference \(\delta = 2.60\).\(^3\) Such data also confirmed the existence of Li in the SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) phosphor. We also could observe two splitting peaks located at 2.55 and \(-0.10\) ppm in the magnifying NMR spectrum (Figure S2), these peaks were ascribed to two different Li sites in the SrLiAl\(_3\)N\(_4\) structure. The \(^27\)Al solid-state NMR spectrum was also measured and presented in Figure S3. Three peaks centered at 114, 100, and 75 ppm were noted: the latter was ascribed to the cluster of AlN\(_4\) weak peak of AlO\(_6\) at 8 ppm,\(^16\) one can conclude the presence of low oxygen content in the SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) phosphor, indicating that SrLiAl\(_3\)N\(_4\):Eu\(^{2+}\) was not stable in air. To determine the valence of the doped Eu, X-ray absorption near-edge structure (XANES) was performed.
The calculated diode emission peak position and width will result in an obvious difference as unimportant. Furthermore, even tiny variations in emission peak position and width will result in an obvious change in the spectral theoretical lumien equivalent because the upper limit sensitivity curve of the human eye exhibits a steep grade in the saturated red spectral range. The temperature-dependent emission spectra overlapped with the human eye response curve (Figure 3d). According to the modified equation of the reference (equation shown in Supporting Information),\textsuperscript{15} we further calculated the theoretical luminous intensity for SrLiAl\textsubscript{3}N\textsubscript{4} has two similar Sr sites (Figure 1b).

For general lighting application, high-power blue LEDs (blue light output > 100 W cm\textsuperscript{-2}) are necessary. However, such a high power inevitably results in the high junction-temperature of the chip, which finally leads to the decline in emission intensity and the shift in the maximum emission wavelength of the phosphor. Therefore, systematically evaluating the thermal quenching behavior and chromaticity stability of the as-synthesized red phosphor SrLiAl\textsubscript{3}N\textsubscript{4}:Eu\textsuperscript{2+} is an important task. First, we focused on the temperature-dependent emission intensity. The relative integrated intensity of SrLiAl\textsubscript{3}N\textsubscript{4}:Eu\textsuperscript{2+} dropped from an initial 100% at 298 K to 93% at 473 K and 88% at 573 K, respectively (Figure 3b). While at 473 and 573 K, the intensities of the peak wavelength (650 nm) were 81% and 71%, respectively. The origin of difference between the integrated intensity and the intensity of 650 nm is the blue shift in the maximum emission wavelength and the broadening of the emission band with the increase in temperature. In fact, in 298–573 K, the peak wavelength shifted from 654 to 646 nm; meanwhile, the spectrum broadened from 62 to 75 nm. This change can also be observed in the temperature-dependent emission spectra for SrLiAl\textsubscript{3}N\textsubscript{4}:Eu\textsuperscript{2+} (Figure 3a). Notably, the peak wavelength and fwhm of temperature-dependent emissions slightly differed from the emission observed at room temperature; the difference is attributed to the measurement of two emissions on different spectro-flurometers, with a slight discrepancy in the spectral response. For this part of the present work, we focused on the trend of the temperature-dependent emission behavior temporarily regarding the difference as unimportant. Furthermore, even tiny variations in emission peak position and width will result in an obvious change in the spectral theoretical lumien equivalent because the upper limit sensitivity curve of the human eye exhibits a steep grade in the saturated red spectral range. The temperature-dependent emission spectra overlapped with the human eye response curve (Figure 3d). According to the modified equation of the reference (equation shown in Supporting Information),\textsuperscript{15} we further calculated the theoretical luminous intensity for SrLiAl\textsubscript{3}N\textsubscript{4}:Eu\textsuperscript{2+} dropped from an initial 100% at 298 K to 93% at 473 K and 88% at 573 K, respectively (Figure 3b). While at 473 and 573 K, the intensities of the peak wavelength (650 nm) were 81% and 71%, respectively. The origin of difference between the integrated intensity and the intensity of 650 nm is the blue shift in the maximum emission wavelength and the broadening of the emission band with the increase in temperature. In fact, in 298–573 K, the peak wavelength shifted from 654 to 646 nm; meanwhile, the spectrum broadened from 62 to 75 nm. This change can also be observed in the temperature-dependent emission spectra for SrLiAl\textsubscript{3}N\textsubscript{4}:Eu\textsuperscript{2+} (Figure 3a). Notably, the peak wavelength and fwhm of temperature-dependent emissions slightly differed from the emission observed at room temperature; the difference is attributed to the measurement of two emissions on different spectro-flurometers, with a slight discrepancy in the spectral response. For this part of the present work, we focused on the trend of the temperature-dependent emission behavior temporarily regarding the difference as unimportant. Furthermore, even tiny variations in emission peak position and width will result in an obvious change in the spectral theoretical lumien equivalent because the upper limit sensitivity curve of the human eye exhibits a steep grade in the saturated red spectral range. The temperature-dependent emission spectra overlapped with the human eye response curve (Figure 3d). According to the modified equation of the reference (equation shown in Supporting Information),\textsuperscript{15} we further calculated the theoretical luminous

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The lumen equivalent monotonously increased with increasing temperature. The broadened width and blue shift of emission are beneficial in increasing the theoretical luminous efficiency because emissions closer to green light at 555 nm result in higher lumen equivalents. All the above-mentioned results indicate that SrLiAl₃N₄:Eu²⁺ has a low thermal quenching behavior. To further assess the chromaticity stability of SrLiAl₃N₄:Eu²⁺, we present the change in chromaticity coordinates in Figure 3c. The chromaticity coordinates shifted to the short wavelength when the temperature changed from room temperature to 373 to 473 and finally 573 K. This trend is in agreement with the results observed in Figure 3a. To further quantitatively describe the variations, we calculated the CIE shift of SrLiAl₃N₄:Eu²⁺ and commercial CaAlSiN₃:Eu²⁺ red phosphor (Figure 3f).₂₀−₂² Results indicate that the SrLiAl₃N₄:Eu²⁺ has a better chromaticity stability than that of commercial red phosphor.

To demonstrate the potential application of the title phosphor, we fabricated the white LEDs using the “red phosphor (SrLiAl₃N₄:Eu²⁺) + yellow phosphor (YAG:Ce³⁺) + blue LED chip” method. Figure 4a,b shows the electroluminescence spectra of the as-fabricated white LEDs (1, 2). Both spectra included three bands peaking at 450, 550, and 650 nm, ascribed to the blue LED chip, commercial YAG:Ce³⁺ phosphor, and the title phosphor, respectively. By employing SrLiAl₃N₄:Eu²⁺ phosphor, we easily fabricated high-CRI (85) white LEDs (Figure 4a). By appropriately adjusting the ratio of yellow phosphor to red phosphor, a warm white light (CCT = 2875 K) with high CRI (Ra = 91.1) was achieved. Furthermore, the R9 index was as high as 68, indicating that the red spectral part was enhanced obviously. As seen in the inset of Figure 4c, the white LEDs (2) emitted warm white light. In addition, the LE was 48.8 and 24.9 lm/W for high-CCT white LEDs and low-CCT white LEDs, respectively. These results validate the SrLiAl₃N₄:Eu²⁺ red phosphor as a promising prospect for use in the fabrication of high-power white LEDs.

4. CONCLUSION

In this paper, we reported the synthesis of a highly stressed narrow-band red-emitting nitride phosphor, SrLiAl₃N₄:Eu²⁺, using Sr₃N₂, Li₃N, Al, and EuN under atmospheric pressure for the first time. This phosphor emitted a red light that peaked at 650 nm with a narrow FWHM of 55 nm under 460 nm excitation. The high thermal stability of the title phosphor, including the thermal quenching behavior and chromaticity stability, was studied in detail. By employing commercial YAG:Ce³⁺ yellow phosphor, SrLiAl₃N₄:Eu²⁺ red phosphor, and blue LED, we successfully fabricated a warm white LEDs with CRI of 91.1 and CCT of 2875 K. All of the results suggested that this narrow-band red-emitting phosphor is a promising candidate for high-power and high-CRI white LEDs. Furthermore, this facile synthesis method is expected to facilitate further investigation of SrLiAl₃N₄:Eu²⁺ toward its actual application and exploring other narrow-band-emitting phosphors. In addition, the analysis results also help reveal the underlying requirements to design Eu²⁺-doped narrow-band-emitting phosphors: first, a rigid and ordering network structure is very important to decrease nonradiative relaxation; second, the replaced cation should have only one crystallographic site and almost the same size as the activator Eu²⁺ to reduce emission overlap and the distortion of coordination polyhedron; third, a high symmetry around the activator site with high coordination number, producing the same distance between the activator and ligand, is favorable for astringing inhomogeneous emission broadening. Last but not least, the long distance between activators and a large distance between the lowest 4f⁶5d¹ excited state of Eu²⁺ and the bottom of the conduction band can effectively avoid the concentration quenching and photoionization effects at high temperature.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b05485.

The methods to calculate the color purity, lumen equivalent, chromaticity shift, and average lifetime were introduced in detail in the Supporting Information. Structural main parameters of the red phosphor SrLiAl₃N₄:Eu²⁺. Powder XRD pattern of SrLiAl₃N₄:Eu²⁺ phosphor. ⁷Li and ²⁷Al solid-state MAS NMR spectra of...
SrLiAl$_3$N$_4$:Eu$^{2+}$ phosphor. Decay curves of SrLiAl$_3$N$_4$:Eu$^{2+}$ phosphor. (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**
*E-mail: rsliu@ntu.edu.tw. Phone: +886-2-33661169. Fax: +886-2-23636359.*

**Notes**
The authors declare no competing financial interest.

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