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and Na⁺ Doping

Tailoring the Luminescent Properties of SrS:Ce³⁺ by Sr-Deficiency

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ACCESS III Metrics & More Article Recommendations SI Supporting Information ABSTRACT: Ce3+-doped SrS phosphors with a charge-compensating Na+ SrS Ce addition were successfully synthesized via a solid-state reaction method, and the Na (host) related X-ray diffraction patterns can be indexed to the rock-salt-like crystal structure of the $Fm\overline{3}m$ space group. SrS: $(Ce^{3+})_x$ (0.005 $\leq x \leq$ 0.05) and SrS: $(Ce^{3+})_{0.01}$ (Na⁺)_y (0.005 $\leq y \leq 0.030$) phosphors were excited by 430 nm UV-Vis light, targeted to the $5d^1 \rightarrow 4f^1$ transition of Ce³⁺. The composition-optimized SrS: 5d $(Ce^{3+})_{0.01}$, $(Na^{+})_{0.015}$ phosphors showed an intense broad emission band at $\lambda =$ 430-700 nm. The doping of Na⁺ was probed by solid-state nuclear magnetic resonance. The 430 nm pumped white light-emitting diode structure fabricated with a combination of SrS:(Ce³⁺)_{0.01},(Na⁺)_{0.015} and Sr₂Si₅N₈:Eu²⁺ phosphors shows a color-rendering index (R_a) of 89.7. The proposed strategy provides new avenues for the design and realization of novel high color quality solid-state LEDs.

1. INTRODUCTION

Phosphor-converted white light-emitting diode (pc-wLED) lighting has acquired incredible accomplishment since the successful invention of the InGaN blue LED by Isamu Akasaki et al., awarded the Nobel Physics Prize in 2014.¹ Presently, pcwLEDs have become an increasingly hot topic due to a wealth of unique advantages, such as environmental friendliness, long lifetime, and tunable colors allowing for a wide utilization in the fields of bioimaging, anticounterfeiting, lighting, medical applications, and many more.^{2–8} Exploring classical phosphors, being the essential ingredient of solid-state lighting emitting diodes (SS-LEDs), has been performed by introducing rare earth (RE) ions into inorganic host materials.⁹⁻¹¹ In the early 1990s, the phosphors of alkali-earth metal sulfides (MgS, CaS, SrS, and BaS) doped with Eu²⁺, Eu³⁺, and Ce³⁺ were extensively studied for cathodoluminescence and electroluminescence displays.^{12,13} A series of commercial CaS:Eu phosphors have recently been investigated as solid-state light sources due to the red emission near 645 nm. SrS is considered as a potential substrate matrix owing to its small vibrational frequencies and narrow band gap energy.^{14,15} The luminescence properties of SrS can be modulated over the entire region of the visible electro-magnetic spectrum when doped with appropriate RE ions. However, conventional synthesis methods of alkaline-earth sulfide compositions, including gassolid diffusion reactions, reverse micelles, metal organic chemical vapor deposition, and solvothermal methods, restricted the large-scale preparation of strontium sulfide and application in white-light LEDs.^{16–18} SrS phosphors were obtained via the gas-solid reaction method by sulfurating alkaline earth-based sulfate, carbonate, and nitrate in N_2 with a H_2S or CS_2 atmosphere.¹⁹ This approach involved toxic gases and thus is prohibited for wider academic investigations and potential industrial applications. Therefore, it is of great importance to find alternative synthesis methods with low cost, easy manipulating, and environmental friendliness.

Additionally, cerium-doped phosphors have gained increased interest due to the excellent photoluminescent properties and their compatibility with different host materials. The $5d^1 \rightarrow 4f^1$ transition of the Ce³⁺ activator is sensitive to the crystal structure and the ion site coordination environment. Ce³⁺-doped samples normally show $5d^1 \rightarrow 4f^1$ emission in the ultraviolet, but in the case of high crystal-field splitting, such as in garnets (Gd₃Al₅O₁₂), visible emission is observed.^{20–23} The emission spectra of Ce³⁺ of garnet series, $Mg_3(Y_{1-y}Gd_y)_2(Ge_{1-z}Si_z)_3O_{12}:Ce^{3+}$ (y = 0-1, x = 0,1), can be modified with variations in the Ce-O bond lengths arising from different dopant concentrations and chemical substitution.²⁴ Alkali metals were used to dope the host matrix with the goal of modulating the Ce³⁺ spectra. However, the doping sites and local environments could not to be investigated directly due to a lack of experimental probes until recently. Solid-state magnetic resonance has been proved to be a highly versatile

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Figure 1. (a) Scheme of synthesis process. (b) X-ray diffractograms of SrS with different doping contents of Ce^{3+} . (c) Rietveld refinement of the SrS with 0.01 Ce^{3+} dopant.

tool to probe the local electronic environment, ground-state electronic structure, defects, and chemical surroundings, providing a powerful alternative to other characterization methods.²⁵⁻³⁰

In this work, Ce³⁺ and Na⁺ are successfully incorporated into SrS, exhibiting broad-band emissions in the wavelength range of $\lambda = 430-700$ nm. The luminescent properties for the target materials were tailored by the doping of Ce³⁺ and Na⁺, which can be easily adjusted to optimize the color-rendering index and chromaticity. X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) were carried out to investigate the local structure–property correlations in the host materials. Afterglow phenomena were observed originating in vacancy defects in the crystalline lattice. SrS:Ce³⁺ and SrS:Ce³⁺,Na⁺ phosphors were fabricated and they showed tunable luminescence properties by the introduction of dopant and defect-involved emissions into single-dopant-activated phosphors under the $\lambda = 430$ nm light excitation appropriate for w-LED.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. Strontium carbonate (SrCO₃, 99.5%), cerium oxide (CeO₂, 99.9%), and sodium carbonate anhydrous (Na₂CO₃, \geq 99.5%) were purchased from Macklin and sulfur flowers (S, 99.999%) were purchased from Aladdin. The commercial red phosphor Sr₂Si₃N₈:Eu was purchased from Shenzhen looking long technology co., LTD. All the chemicals were used without further purification.

2.2. Synthesis of SrS Phosphors. A series of $SrS:(Ce^{3+})_x$ phosphors with different Ce^{3+} contents (x = 0.005-0.05) were synthesized by employing a solid-state reaction method. The experimental steps were as follows (Figure 1a): $SrCO_3$, CeO_2 , and S were ground with 1:*x*:2.5 mole ratio in the mortar for 30 min to get uniform mixtures. Then, the mixtures were loaded in a large alumina crucible with a thin layer of carbon powder and sintered at 1100 °C for 2 h in a high-temperature box furnace under the air atmosphere. Finally, the obtained samples were cooled to room temperature (RT) in the furnace and were reground for 5 min for further measurements. Other samples were based on the same method of preparation.

2.3. Characterizations. Powder X-ray diffraction (PXRD) patterns for crystal structure determination were recorded by using an XRD diffractometer (PANalytical Empyrean) operating with Cu

 $K\alpha$ radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA. Rietveld refinement was conducted by employing Fullprof software (64). The particle morphology was observed by field emission scanning electron microscopy (FE-SEM; JSM-7900F) and the elemental mapping was carried out using energy-dispersive X-ray spectroscopy (EDS) attached to the FE-SEM device. The chemical states of the constituent elements were obtained by X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250Xi), and the carbon peak fixed at 284.8 eV was applied as a reference to correct other peak binding energy position. The photoluminescence emission (PL) and excitation (PLE) spectra at RT of all samples were recorded with a lifetime and steady-state spectrometer (FLS980, Edinburgh Instruments Ltd.) equipped with a Xe lamp.

Solid-state NMR was performed on a Bruker Avance III-400 spectrometer with a static field of 9.2 T. The Na-doped SrS (Ce) material was homogeneously filled in 4.0 mm zirconia rotor and was spun at 8 kHz. An echo pulse with 1.8 μ s as 90° was applied. The recycle delay was set as 0.5 s and total 4 k transitions were accumulated for reasonable signal-averaging. The peak of 1 mol·L⁻¹ of NaCl (aq) at 0 ppm is used as an external chemical shift reference.

W-LED structures were fabricated with the commercial red phosphor $Sr_2Si_5N_8$:Eu and a LED chips (λ = 430 nm). The phosphors were mixed with a commercial AB silicone glue (glue A: hardener B = 1:4, AB silicone glue: as-synthesized phosphors: red phosphors = 10:3:1). The obtained phosphor-glue mixture was coated on the LED chips and then cured at 100 °C for 1 h. The properties of the fabricated w-LEDs were measured by an HAAS-2000 photoelectric measuring system (380–780 nm, EVERFINE, China). The forward bias current was 100 mA.

3. RESULTS AND DISCUSSION

The micrometer-sized (μ m) phosphors of SrS:(Ce³⁺)_x (x = 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mol %) with the nominal composition were synthesized via high-temperature solid-state reaction methods.^{31,32} PXRD patterns of the products are shown in Figure 1b. All major diffraction peaks are attributed to a rock-salt-like structure of SrS and can be well indexed with an $Fm\overline{3}m$ space group, consistent with the standard diffraction patterns of this material class (PDF card no.08-0489).³³ No extra phases were found, indicating that the doping of Ce³⁺ in the materials does not affect the SrS long-range crystalline order. The peaks between $2\theta = 50$ and 53° degrees show a small right shift for the Ce³⁺-doped SrS when compared with



Figure 2. (a) Full XPS spectrum of SrS with x = 0.01 Ce³⁺ dopant. (b) High-resolution spectra of S 2p and (c) Sr 3d.



Figure 3. (a) PL spectra of $SrS:(Ce^{3+})_x$ and the inset are photos of samples under 365 nm UV lamp and with afterglow luminescence. (b) PLE spectra of $SrS:(Ce^{3+})_x$. (c,d) Dependence of PL maximum position and PL peak intensity on Ce concentration of $SrS:(Ce^{3+})_{x^3}$ respectively. The curves in (c,d) are guided by eye.

the pure material (Figure S1). We suppose that this effect is caused by the lattice expansion due to Ce³⁺ incorporation. To further understand the phase structure and site occupation of Ce³⁺ ions, Rietveld refinement was performed for the sample with x = 0.01 Ce³⁺ doped (SrS:1.0 mol % Ce³⁺, as shown in Figure 1c). The unit cell volume varies nonlinearly with the increase in RE element doping concentration (Figure S1), suggesting that the Ce³⁺ ion could partially occupy atomic sites of the Sr²⁺ ion.³⁴⁻³⁶ Reliability factors including Bragg *R*-pattern factor ($R_p = 2.488\%$), weighted-profile *R* factor ($R_{wp} = 1.362\%$), and goodness-of-fit parameter ($\chi^2 = 1.27$) evidence the excellent quality and the dependability of the refinement's data. The refined cell parameters are a = b = c = 6.016(3) Å, $\alpha = \beta = \gamma = 90^\circ$, and V = 217.73(2) Å³, confirming a cubic rock-

salt structure of the as-prepared particle phosphors. The obtained cell parameter is slightly smaller than that of standard value (a = b = c = 6.063 Å, $\alpha = \beta = \gamma = 90^{\circ}$, and V = 222.93 Å³). The shrinkage of the crystal structure with Ce³⁺ doping could be attributed to two reasons: (1) a smaller size of Ce³⁺ ions (1.01Å, CN = 6) occupying the bigger Sr²⁺ sites (1.18 Å, CN = 6). (2) Charge difference between Ce³⁺ and Sr²⁺ would generate the cation vacancies in the process of substitution, which can enhance the degree of crystal lattice shrinkage (Figure S1).³⁷

In order to characterize the morphology and elemental composition of the synthesized $SrS:(Ce^{3+})_{0.01}$ phosphor, FE-SEM and EDS were performed, as shown in Figure S2. The SEM images show a homogeneous distribution with an average



Figure 4. (a) X-ray diffractograms of SrS:1 mol % Ce^{3+} with different doping contents of Na⁺. (b) Solid-state ²³Na-NMR spectrum of SrS: $(Ce^{3+})_{0.01}/(Na^+)_{0.005}$. Asterisks indicate spinning side bands. (c) Zoomed in spectral region around the centroid of the spectrum. The experimental data (blue line) was simulated using the algorithm of Hughes and Harris et al.⁵⁰ The shift position and relative occupancy are noted next to the corresponding Na assignments.

particle size of 50 μ m. The smooth surface would be beneficial to the luminescent properties and incorporation into LED packages. The elemental mapping images conducted on a randomly selected site show a uniform distribution of Sr, S, and Ce within the phosphor particles and the average atomic ratio of Sr:S is close to unity (Figure S3), which is in good agreement with chemically anticipated stoichiometry.

XPS analysis was performed to investigate the chemical nature of the particle surface and get further insights into the electron effect of the doped phosphor host matrix. Figure 2a shows XPS spectrum of SrS: $(Ce^{3+})_{0,01}$ in the binding energy range of E = 0-900 eV, which indicates the presence of Sr, S, C, and O in the system. Due to the low concentration of the Ce³⁺ dopant, a corresponding cerium signal was below the detection limit. The C 1s peak (E = 284.8 eV) corresponds to C–C, caused by adventitious carbon. The O 1s signal (E = 531eV) is likely caused by carbon dioxide absorption from air. The high-resolution XPS spectra recorded for S²⁻ and Sr²⁺ signals are shown in Figure 2b,c, respectively. S 2p doublet is composed of four peaks at E = 168.6, 166.7, 162.1, and 160.1 eV.38-40 Careful analysis of Sr 3d shows one doublet located at E = 135.1 eV and 133.38 eV with an energy difference of 1.7 eV, associated to Sr $3d_{3/2}$ and Sr $3d_{5/2}$, respectively.⁴¹

The PL and PLE spectra of the synthesized SrS with variable concentrations of Ce³⁺ were investigated at RT to characterize the photophysical properties of our products. As shown in Figure 3a, the SrS: $(Ce^{3+})_x$ phosphors exhibit two overlapping signals at $\lambda \approx 495$ nm and a minor shoulder centered at $\lambda \approx$ 530 nm under excitation at $\lambda \approx 276$ nm. It is due to the typical Ce^{3+} emission from the 5d¹ excited energy level to the 4f¹ ground energy level.^{31,42} The corresponding PLE spectrum (Figure 3b) monitored at $\lambda \approx 536$ nm possesses a broad band in the region of $\lambda \approx 250-500$ nm, accompanied by a weak band at $\lambda \approx 280$ nm and an intense band at $\lambda \approx 430$ nm. The former band (280 nm) can be attributed to the effective host band-band transition, whereas the latter (430 nm) is related to the transitions to the ${}^{2}T_{2g}$ and ${}^{2}E_{g}$ states of the 5d electronic manifold of octahedrally coordinated Ce^{3+} , replacing the Sr^{2+} ion in the SrS lattice.^{42,43} We conclude that SrS doped with Ce³⁺ can be sufficiently excited by both ultraviolet and blue light and shows its potential for LED fabrication.

Meanwhile, when doping a certain amount of the Ce, the PL peak maximum exhibits a slight red shift from 491 to 500 nm and the PL peak amplitude significantly decreases (Figure 3c,d, respectively). These effects are associated to an increased defect density in the crystal lattice and the migration of Ce³⁺ ions during the crystallization process. In stoichiometric SrS, the substitution of Ce³⁺ at the Sr²⁺ site (Ce_{Sr}) is believed to be compensated by a Sr²⁺ deficiency to form a charge-neutral Ce_{Sr}-V_{Sr} complex. With the increase in Ce³⁺ concentration, the Sr²⁺ deficiencies into SrS:Ce³⁺ were insufficient to fully compensate the excess negative charge of Ce_{Sr}, leading to a decreased emission intensity.^{44,45} Notably, a long afterglow is observed by the naked eyes and lasts about several seconds in the single Ce³⁺-doped and double-doped phosphors (Figures 3a and S9), which further confirms the presence of Sr²⁺ vacancy.

Within the doping range of the study, 0.5 mol % Ce³⁺ is considered the optimal doping level realized with the employed solid-state reaction method. Hence, it is assumed that the likelihood of energy transfer among the Ce³⁺ ions increases with the increase in the concentration of Ce³⁺ ions in the host matrix.¹³ Judging by Blasse's proposal 1, the critical distance of energy transfer (R_c) is calculated as 27.50 Å.

$$R_{\rm c} = 2 \left(\frac{3V}{4\pi x_{\rm c} N}\right)^{1/3} \tag{1}$$

where *V* is the unit cell volume, *N* is the number of total Ce³⁺ sites per unit cell and x_c is the critical concentration of the activator ions. In SrS, V = 217.73 Å³, N = 4, and the critical concentration, x_c , is about 0.005. As the value of R_c is over 5Å, the exchange interaction has no accountable effect for nonradiative energy transfer processes between adjacent Ce³⁺ ions in the matrix. Thus, the concentration quenching mechanism in Ce³⁺-doped SrS phosphors may have happened due to multipole–multipole interactions which are responsible for the energy transfer of forbidden transitions.^{13,46}

The Commission International de L'Eclairage (CIE) 1931 chromaticity coordinates calculated from the emission spectra of $SrS:(Ce^{3+})_x$ phosphors are shown in Figure S4. The emission color is adjusted from green to green–yellow with the



Figure 5. (a) PL spectra of SrS:1mol%Ce³⁺,yNa⁺. (b,c) Dependence of PL maximum position and peak intensity on Na concentration of SrS:1mol%Ce³⁺,yNa⁺, respectively. These curves in (b,c) are guided by eye. (d) PLE spectra of SrS:1mol%Ce³⁺,yNa⁺. (e) The crystal structure models of SrS:Ce³⁺ and SrS:Ce³⁺,Na⁺ and schematic energy level diagram of the SrS:Ce³⁺ phosphors.

increase in Ce³⁺ concentration, suggesting increased crystalfield splitting of the Ce-5d energy levels by Ce_{Sr} and V_{Sr} substitution, while the corresponding CIE chromaticity coordinates ranged from (0.2465, 0.4798) to (0.3269, 0.5173).⁴⁷ Compared with other green phosphors, the value along *y* axis in the CIE chromaticity is larger than that of (Ba_{1.2}Ca_{0.8-x}Eu_x) SiO₄ and Ca₂YHf₂Al₃O₁₂:Ce³⁺, Tb³⁺. Thus, the as-prepared phosphors have a greater luminescence and show more yellow color tune.^{48,49} The CIE color coordinates and correlated color temperature (CCT) are listed in Table S1. These results indicate that the phosphors can exhibit tunable properties for various SS-LED applications and are highly promising candidates for general lighting devices.

In order to sustain electric neutrality for enhancing the luminescent properties, Na⁺ alkali-metal ions were introduced into 1 mol % Ce³⁺-based phosphors SrS. The concentration of Na⁺ varies from y = 0.5 to y = 3.0 mol % with the help of conventional solid-state reaction method.³⁴ As displayed in Figure 4a, the major reflections in our diffraction patterns can match well with those of base SrS patterns, demonstrating that the introduction of Ce³⁺ and Na⁺ does not distort the long-range crystal structure of the host lattice. Similar to the data shown in Figure 1, higher angle shifts are observed for the diffraction peaks between $2\theta = 50$ and 53° degrees after the doping with Na⁺ ions (Figure S6). According to Bragg's law 2 and Scherrer's formula 3, we conclude that the structure change caused by Na⁺ doping is negligible.

$$n\lambda = 2d\,\sin\theta\tag{2}$$

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{3}$$

The static ²³Na-NMR spectrum (envelope over the MAS spectrum shown in Figure 4b) displays a broad signal of 1600

ppm (about 180 kHz). Spectral simulation of the centroid region of the MAS spectrum [at $(\omega - \omega_0) = \pm 60$ ppm] reveals one nearly axially symmetric coordination site of sodium ions with an isotropic frequency shift of $(\omega - \omega_0)_{iso} = 7.9(2)$ ppm and a pronounced anisotropy of 10.5(3) ppm. Additionally, we observe a second very weak signal at about $(\omega - \omega_0)_{iso} = -13.5(8)$ ppm contributing only up to 8% of the total signal intensity and may be originating in surface ions. Further studies will be conducted to illuminate this possibility.

The poor fit quality of the main peak may be caused by a superposition of both angular-dependent chemical and paramagnetic shift interactions influencing the resonance frequency distribution of non-coaligned principal axis systems.^{50,51} The NMR results indicate that Na is successfully doped into the lattice of SrS, rather than the formation of Na₂S.²⁴

The representative FE-SEM images and EDS mapping results of Ce³⁺-doped SrS with 0.5 mol % Na are displayed in Figure S6. From the SEM images, it is demonstrated that the sample composed of anomalous and aggregated particles with a size of $5-30 \ \mu\text{m}$ (Figure S6a,b). To investigate the chemical composition of the particles, the EDS spectra confirms the uniform distribution of Sr, S, Ce, and Na, suggesting successful doping of Ce³⁺ and Na⁺. Moreover, the elemental distribution was also investigated by EDS, which yields an average Sr/S atomic molar ratio of ~100% (Figures S6c-e and S7), in accordance with our XRD patterns. Ce and Na are homogeneously distributed exhibiting low intensities in the target sample (Figure S6f,g).

It is widely acknowledged that the phosphor with an efficient charge compensation shows enhanced luminescent intensity. $^{52-56}$ In addition, the ionic radius of the charge compensator plays a vital role in the host lattice. In the case of SrS:Ce³⁺, the excess of positive charge caused by Ce³⁺ in the matrix is well compensated with Na⁺ (Na⁺ + Ce³⁺ $\rightarrow 2Sr^{2+}$)

(1.18 Å). To further explore the effect of Na⁺ in the Ce³⁺based material, the PL and PLE spectra were assessed. As given in Figure 5a, all the PL spectra of Na⁺-doped SrS: $(Ce^{3+})_{0.01}$ powders show broad-band extending over the wavelengths λ = 400-700 nm under 276 nm UV light excitation. In Figure 5d, monitored at 486 nm, the PLE spectra of SrS: $(Ce^{3+})_{0.01}$, $(Na^+)_{\nu}$ samples show a signal with weak amplitude at $\lambda \approx 430$ nm and a strong signal with large amplitude at $\lambda \approx 276$ nm, which is possibly associated to the 4f \rightarrow 5d transitions of Ce³⁺ in an octahedral crystal field. Figure S8 shows a comparison of obtained PL spectra of SrS: $(Ce^{3+})_{0.01}$, $(Na^+)_y$, $(0.005 \le y \le 10^{-1})_y$ 0.03). From the comparison of the spectra, photoluminescence is almost independent of Na⁺ doping, despite minor fluctuations in signal intensities. The PL peak amplitudes were found to increase with the Na^+ concentration of [0, 1.5]mol % and decreases upon further increase in Na⁺ concentration, as presented in Figure 5b,c. Significantly, with the increase in Na⁺ content, the PL intensity is enhanced and the peak is blue-shifted up to the maximum of 1.5 mol % Na⁺ doping. In a previous report, Tong et al. found the incorporation of the charge compensator onto the Sr lattice site of SrS:Ce³⁺ minimizes vacancy formation, which can produce a blue shift in the PL spectra.⁵⁷ In the same vein, as Na^+-S^{2-} bond lengths in SrS are smaller than that in $Sr^{2+}-S^{2-}$ bond lengths, this site-perturbation should be more pronounced when the concentration of Na⁺ is higher than that of the pristine samples (y = 0). Thus, the red shift of the emission spectrum occurs in samples with higher doping concentration of Na⁺, as pointed out previously.⁵⁸ Based on the results, doping mechanism and possible electronic transitions are summarized in Figure 5e. As seen in Figure S9, there is no significant difference of the emission color, which changes only from cyan to green as Na⁺ ion concentration is gradually increased. The CIE color coordinates and CCT are listed in Table S2. To demonstrate the luminous effect of the asprepared phosphors for potential practical application, SrS: $(Ce^{3+})_{0.01}$, $(Na^+)_{0.015}$ was incorporated in a w-LED lamp. As a specific package process shown in the Supporting Information, a commercial blue InGaN chip ($\lambda_{em} \approx 430$ nm) was used for packaging experiment.

Figure 6 shows the emission spectrum of packaged lamp driven by a 99.95 mA current at 2.821 V, which consists of the green and yellow light from the as-prepared phosphors. The red light was provided by the nitride phosphor and the R_a



Figure 6. PL spectrum and photos of the w-LED device fabricated with as-prepared phosphors, the commercial red phosphor $Sr_2Si_5N_8{:}Eu^{2+}$ and an LED chips ($\lambda\approx430$ nm).

increased from 60 to 89.7. As shown in Figure S9, the corresponding CIE color coordinates of the packaged w-LEDs lamp are calculated to be (0.3108, 0.3458), which are similar to ideal white chromaticity coordinates (0.3333, 0.3333) of the National Television Standard Committee system. The inset photo in Figure 6 displays an intense white light emitting for the packaged lamp with CCT = 4823 K and a high CRI value of 87.0. Moreover, the afterglow phosphor shows large flexibility in alternating current (AC) and can completely eliminate the use of an AC/direct current converter required in conventional LED lighting technologies, thereby leading to reduced cost and further enhanced efficiency.^{59,60}

4. CONCLUSIONS

We successfully designed and synthesized SrS: (Ce^{3+}) , (Na^+) phosphor exhibiting a broad emission band in the wavelength range of $\lambda = 430-700$ nm via a facile solid-state reaction method. By designing Na-substituted and Sr-deficient SrS: (Ce^{3+}) , (Na^+) to realize charge-compensating defects, higher emission intensity and afterglow phenomena were generated. The luminescence properties were modulated by modification of the crystal structure via doping with RE metal ions and thus influencing crystal-field splitting at the octahedral coordination site of the cerium ions.

The well-packaged w-LED lamp exhibits a warm white light (4823 K) and a high CRI (R_a) value of 87.0 (89.7), promising the application of SrS:(Ce³⁺) phosphors as blue-excited greenemitting components for w-LEDs. The present demonstration of design strategy and characterization methods can also initiate further exploration to design various advanced phosphors with tunable spectra and improved performance for w-LEDs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c04016.

Additional XRD; SEM images and elemental mapping of Ce- and Na-doped materials; three-dimensional drafting of PL spectra of $SrS:(Ce^{3+})_{0.01}/(Na^{+})_{y}$; and CIE chromaticity diagram and photographs of $SrS:(Ce^{3+})_{x,y}$ $(Na^{+})_{y}$ (PDF)

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Author Contributions

S.C., X.S., and K.W. performed material synthesis and structure characterizations. L.X. and Q.W. collected NMR data. G.B. and G.L. contributed to structural determination and discussion. T.M. helped with NMR data simulation and interpretation. J.F. and M.T. led the project. All authors contributed to the manuscript and are involved in the discussion.

Notes

The authors declare no competing financial interest.

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