Design of a Yellow-Emitting Phosphor with Enhanced Red Emission via Valence State-control for Warm White LEDs Application

Jian Chen¹, Yangai Liu¹, Lefu Mei¹, Peng Peng², Qijin Cheng³ & Haikun Liu¹

The phosphor-converted warm W-LED have being rapidly developed due to the stringent requirements of general illumination. Here, we utilized a strategy to synergistically enhance the red region and emission intensity of novel Eu-activated yellow-emitting LaSiO₂N phosphors. This was realized by predicting optimum crystal structure, and governing the concentration of doping ions as well as preparation temperature. By using these straightforward methods, we were able to vary the valence to enhance the red region and improve the quantum efficiency of LaSiO₂N phosphor. The warm W-LED lamp fabricated with this red region enhanced LaSiO₂N:Eu phosphor exhibited high CRI (Ra = 86), suitable CCT (5783 K) and CIE chromaticity (0.33, 0.36), indicating this synergistically enhanced strategy could be used for design of yellow-emitting phosphor materials to obtain warm W-LEDs.

Due to the deficiency of red color, the cool and bluish-white light LEDs (typically a blue-light LED chip coupled with yellow-emitting YAG: Ce³⁺ phosphor) with high correlated color temperature (CCT) and low color rendering index (CRI) are gradually replaced by blue, green and red (RGB)-emitting phosphors with a UV/NUV chip. However, high cost and poor luminous efficiency of RGB-emitting phosphor became the main obstacles of their popularization because of self-adsorption occurring among these phosphor particles. Currently, white LEDs (W-LED) packaged with UV chips (365–420 nm) with mixed blue and yellow-red emitting phosphors have attracted much attention because of their high CRI, tunable CCT and CIE chromaticity coordinates. Therefore, designing and developing tunable yellow-red emitting phosphors which can be effectively excited with NUV light are in great demand for W-LED industry.

Currently, La–Si–O–N system doped with Ce³⁺ ions has been widely reported as blue phosphors for the application in solid-state lighting, fluorescent lamps or plasma display panels (PDPs). The emission properties of this La–Si–O–N system doped with Ce³⁺ strongly depend on Si/La and N/O ratios, because the 5d electrons of Ce³⁺ ions are unprotected and sensitive to the change of the strength of crystal field and covalency. According to the crystallographic examination for an equal amount of Ce³⁺ substitution, the degree of covalency increased in a sequence of La₅Si₃O₁₂N < La₄Si₂O₇N₂ < La₂Si₆O₃N₈ < LaSiO₂N₁₆. As supported by Dorenbos, the emission position depended on nephelauxetic effect, crystal-field splitting (CFS), and Stokes shift. Herein, Eu²⁺ ions in LaSiO₂N should have stronger nephelauxetic effect due to its high covalency, compared with other La–Si–O–N system compounds. This effect would shift the centroid of the 5d band of Eu²⁺ ions to lower energy and result in the redshift of emission peak. Meanwhile, the higher formal charge of N³⁻ compared with O²⁻ makes the CFS become larger, and the rigid lattice would lead to a smaller Stokes shift. Thus, the LaSiO₂N doped with lanthanide, especially Eu²⁺, may emit long-wave bands. But until now, the Eu²⁺ phospholuminescence in La–Si–O–N system has been rarely reported due to the charge mismatch of Eu²⁺ and La³⁺. However, in our recent experiment, we observed the Eu²⁺⁺⁺ phospholuminescence in LaSiO₂N, and this novel LaSiO₂N: Eu phosphor, as expected, exhibited broad emitting in yellow region. Further, we designed a strategy to cooperatively enhance the red region and emission intensity of this phosphor via altering the concentration of doping ions and preparation temperature for high CRI warm W-LED application. The red region enhancements were caused by...
115.87 nm which was larger than that of YAG phosphor (91.65 nm), indicating that the synthesized phosphor here excitation peaked at 365 nm ranging from 250–500 nm, which can be attributed to the 4f 7(8S7/2)–4f 65d1 transition of the LaSiO2N:0.01Eu phosphor prepared at 1500 °C. The LaSiO2N crystallizes as a hexagonal structure not significantly influencing its crystal structure.

The X-ray diffraction. As the Fig. 1 illustrated, all the diffraction peaks matched well with the standard pattern (JCPDS 71–1115) of LaSiO2N, demonstrating that the doping of Eu ions and the increased preparation temperature did not significantly influence its crystal structure.

Figure 1. XRD patterns of as-synthesized LaSiO2N:Eu phosphors, LaSiO2N host and the standard pattern (JCPDS 71–1115) of LaSiO2N.

Results and Discussion
The phase purity of the as-prepared LaSiO2N:Eu phosphors and LaSiO2N host were substantiated by powder X-ray diffraction. As the Fig. 1 illustrated, all the diffraction peaks matched well with the standard pattern (JCPDS 71–1115) of LaSiO2N, demonstrating that the doping of Eu ions and the increased preparation temperature did not significantly influence its crystal structure.

As shown in Fig. 2a, The PLE spectrum of LaSiO2N:0.01Eu monitored at 554 nm was composed of a broad excitation peak at 365 nm ranging from 250–500 nm; which can be attributed to the 4f 7(8S7/2)–4f 65d1 transition of Eu2+ ions20, and matched well with the emission of commercial N-UV chip (365–420 nm). The reduction of Eu3+ to Eu2+ in the trivalent La site can be explained with the charge compensating defect in the first anion (O2−) ion coordination shell17. The PL spectrum of LaSiO2N:0.01Eu under 365 nm light excitation exhibited a broad yellow band from 450 to 750 nm peaked at 554 nm with a full width at half-maximum (FWHM) of 115.87 nm which was larger than that of YAG phosphor (91.65 nm), indicating that the synthesized phosphor here is a suitable yellow-emitting phosphor candidate for W-LED application.

Figure 2b depicts the Eu concentration dependent PL spectra of LaSiO2N:xEu (x = 0.01, 0.02, 0.04, 0.06, 0.08) phosphors with a 365 nm excitation. It is noteworthy that the shoulder peaks at 596 nm, 614 nm and 660 nm arose increasingly along with the increased Eu concentration. These shoulder peaks are reasonable to attribute to the unreduced Eu3+ ions and can be assigned to 4f–4f transitions of Eu3+ 6D5/2–F7/2, 5/2, 3/2, 1/2(J = 1, 2 and 3))21. As the doping concentration of Eu increased to 6 mol%, the emission intensity reached the maximum and then declined dramatically with a further increase of concentration. Generally, the declined intensity with increased concentration is caused by the concentration quenching effect22. Such effect is mainly caused by the energy consumption via energy transfer from one activator to another23. When the concentration of Eu increased gradually, the interatomic distance between the two Eu ions reduced, and the energy transfer rate between Eu2+–Eu3+ as well as the probability of energy transfer to luminescent killer sites increased24. Simultaneously, the interaction was more intensive with the reduction of interatomic distance. As a result, the 5d band of Eu3+ ion decreased and led to the redshift of emission peak25. As depicted in Fig. 2b, an obvious redshift of emission peak occurred, indicating the intensive interaction between the identical activators26. However, as shown in Fig. 3, the decay curves of LaSiO2N:xEu (x = 0.01–0.08) monitored at 565 nm obviously consist of two lifetimes and all decay curves could be well fitted via the second-order exponential equation27:

\[ I(t) = A_1 \exp(-t/\tau_1) + A_2(-t/\tau_2) \] (1)

where \( I \) means the luminescence intensity; \( A_1 \) and \( A_2 \) are constants; \( t \) is time; and \( \tau_1 \) and \( \tau_2 \) are the lifetimes for the exponential components. As previous researches report that there is only one single La site can be substituted by Eu ion14,16. Thus, the existence of two lifetimes may due to the two kinds of decay forms for Eu2+ one is the process of electrons from the excited state to ground state; the other is the energy transfer process between Eu2+
and Eu$^{3+}$ because of the coexisting of Eu$^{2+}$ and Eu$^{3+}$. The average lifetime $\tau^*$ could be reckoned according to the following equation:

$$\tau^* = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

(2)

based on eqs 1 and 2, the $\tau^*$ can be estimated to 2.92, 2.27, 1.87, 1.58, and 1.17 $\mu$s for LaSiO$_2$N$_3$:Eu$^3+ (x = 0.01, 0.02, 0.04, 0.06$ and 0.08, respectively. The donor decay times decreased as Eu concentrations increased, indicating the existence of energy transfer processes$^{28,29}$. Therefore, the phenomenon of declined intensity in LaSiO$_2$N$_3$:Eu might both result from the energy transfer between Eu$^{2+}$-Eu$^{2+}$ and Eu$^{2+}$-Eu$^{3+}$.

The excitation spectra of LaSiO$_2$N$_3$:Eu$^3+$ were covered by that of Eu$^{3+}$, the charge-transfer state (CTS) could be identified from the excitation spectra of LaSiO$_2$N$_3$:Eu$^3+$ under different emission features at 565 nm, 596 nm, 615 nm and 660 nm. The relative intensity
of shoulder peak at around 300 nm increased from 565 nm to 660 nm excitation, suggesting it played a key role in generation of the Eu$^{3+}$ emission. Theoretically, charge-transfer state (CTS) or the energy transfer from host lattice (HL) to Eu$^{3+}$ can generate this shoulder peak. For detailed investigation of the source of the shoulder peak, the diffuse reflectance spectra (DRS) of LaSiO$_2$N host and LaSiO$_2$N:0.06Eu (prepared at 1500°C and 1550°C). The inset shows the absorption spectrum of LaSiO$_2$N host calculated using the Kubelka-Munk equation.

Figure 5. The schematic illustration of the mechanism of red enhanced Yellow-emitting LaSiO$_2$N:Eu phosphor. PLE ($\lambda_{em}=565$ nm, 596 nm, 617 nm, 660 nm) spectra of the LaSiO$_2$N:0.06Eu phosphors (prepared at 1550°C), and PL ($\lambda_{ex}=365$ nm) spectra of the LaSiO$_2$N:0.06Eu phosphors as a function of the preparation temperature (1500°C, 1525°C, and 1550°C).
(325 nm) from Eu²⁺ emission feature excitation to that of Eu³⁺ also proved the shoulder peak derived from CTS. It is interesting that not only all the emission intensities were enhanced through the increase of the preparation temperature, but also the relative intensity of Eu³⁺ characteristic peak was enhanced compared with that of Eu²⁺. One of reason for the increase of holistic emission intensity may be due to grain growth and the increased degree of crystallization at a higher preparation temperature. It can be substantiated by the micro-morphology of the crystalline LaSiO₂N:0.06Eu phosphors which were observed via SEM, TEM and XRD Refinement. As depicted in Fig. 6, the particles prepared at 1500 °C (Fig. 6a,b) had irregular morphology with the diameters ranging from 0.3 to 0.8 μm. When the preparation temperature increased, the edges and corners of irregular particles became clear, and a dramatic increase in particle sizes was observed (Fig. 6c,d). In addition, a mass of primary crystals reunited to be particles, and the obvious “sintering necks” between primary crystals suggested that grain growth occurred during the process of synthesis. The typical TEM images were illustrated in Figure S1 to further prove the grain growth. After Jade software refined, the relative crystallinity of LaSiO₂N:0.06Eu prepared at 1500 °C and 1550 °C were estimated about 82.38% and 89.91%, respectively, demonstrating the increased degree of crystallization at a higher preparation temperature.

To compare the ratio changing of Eu²⁺ and Eu³⁺, the high-resolution XPS spectra at the Eu 3d of LaSiO₂N:0.06Eu phosphors prepared at 1500 °C, 1525 °C, and 1550 °C were detected, respectively. As exhibited in Fig. 7, two peaks were found at around 1128 eV and 1135 eV, and the shapes as well as binding energies of the Eu3d signals in LaSiO₂N:0.06Eu agreed well with the signals of Eu²⁺ 3d₅/₂ and Eu³⁺ 3d₅/₂, respectively, indicating the existence of Eu²⁺ and Eu³⁺ ions. Additionally, the relative intensity of Eu³⁺ 3d₅/₂ signals was gradually decreased with the increased preparation temperature, revealing the promotion of reduction process of Eu³⁺. This may due to the amount of thermal defects increased with the increasing preparation temperatures, which could charge compensate the Eu²⁺ in the La³⁺ site and improved the reduction from Eu³⁺ to Eu²⁺. Thus, the increase of Eu²⁺ concentration may be a reason for the enhanced emission intensity of Eu²⁺. However, decreased ratio of Eu³⁺ concentration compared with Eu²⁺ was inconsistent with the enhanced emission intensity of Eu³⁺. Hence, other assistance might be involved to contribute the characteristic emissions of Eu³⁺ in LaSiO₂N.

As illustrated in Fig. 8, the PLE (λᵥ = 596 nm) spectra of the LaSiO₂N:0.06Eu phosphors prepared at 1500 °C, 1525 °C, and 1550 °C were deconvoluted into three Gaussian components, respectively. The relative intensity of CTS (fit peak 3) was enhanced, indicating that the charge transfer from the O²⁻ to Eu³⁺ was enhanced and more efficient with the increasing preparation temperatures. This phenomenon can be explained based on the increase of oxygen vacancies (Vₐ) with the increase of nonequivalent substitution of La³⁺ by Eu²⁺ in the host. These Vₐ might act as sensitzers for the energy transfer from host to Eu³⁺ ion due to the strong mixing of charge transfer states. Thus, the relative emission of Eu³⁺ was enhanced, and the red region of this yellow emitting phosphor was promoted. Meanwhile, an obviously redshift of CTS occurred as the preparation temperature increased, which can be attributed to the increase of Eu³⁺-O²⁻ bond length. Since the Eu²⁺ ions have smaller...
Electronegativity than that of Eu° ions, the Eu–O bond strength became weaker with increasing concentration of Eu°, resulting in weakening of bond strength. Hence the Eu°–O° bond length became longer. As reported by Lin et al., the longer the Eu-O bond, the shorter the energy difference between the 4f and O 2p electrons, and the lower energy position of the CTB. Additionally, the coordination number of Eu° was reduced because the V o increased with an increase of the Eu° content in the host, which caused the formation of a centroid of the 5d state at a lower level. Thus, as shown in Fig. 8, the 5d excitation band (fit peak 2 and 3) red shifted and the overlapping between PLE of 596 nm and PL enlarged, indicating that the energy transfer ratio between Eu° and the 5D0 level of Eu° was enhanced. The energy transfer mode between Eu° and Eu° in LaSiO2N: Eu was proposed in Fig. 9. Under the NUV light excitation, Eu° was excited from the ground state 4f 7(8S7/2) to the excited state 4f 65d1. Partial energy relaxed to the ground state through the inherent transition of Eu°, generating a yellow light emission; the rest of energy transferred to the nearest level 5D0 of Eu°, and then 597 nm, 617 nm, 660 nm and 707 nm emissions appeared by a transition to the 7Fj (j = 1, 2, 3 and 4) ground state. With the increase of the preparation temperature, the depressed 5d level showed more overlapping with the 5D0 of Eu°, resulting in the enhancement of the energy transfer between the Eu° and Eu°. The increased emission peak position from 550 nm at 1500 °C to 565 nm at 1550 °C and FWHM of emission peak from 116 nm at 1500 °C to 120 nm at 1550 °C also verified the redshift of 5d level. The decay curves of LaSiO2N:0.06Eu prepared at different temperatures monitored at 565 nm were depicted in Fig. 10. All decay curves also could be well fitted via the second-order exponential equation and the lifetimes were estimated 1.58, 1.23, and 0.96 μs for LaSiO2N:0.06Eu prepared at 1500 °C, 1525 °C, and 1550 °C, respectively, demonstrating the existence of energy transfer. Consequently, via the increase of preparation temperature, the holistic emission intensity was enhanced owe to the increased crystallinity and reduction process. The relative emission intensity of Eu° was also increased due to the enhancement of the energy transfer. As a result, the red region of yellow emitting LaSiO2N: Eu phosphor was successfully enhanced.
The quantum efficiency of phosphors, which is an important technological parameter for practical application, were also been compared. The internal quantum efficiencies (IQE) of LaSiO$_2$N:0.06Eu prepared at different temperature were measured and calculated by the following equations:

$$\eta_{\text{QE}} = \frac{\int L_S}{\int E_R + \int E_S}$$  (3)

where $L_S$ represents the luminescence emission spectrum of the sample; $E_R$ is the spectrum of the excitation light from the empty integrated sphere (without the sample); $E_S$ means the excitation spectrum for exciting the sample. As given in Figure S2, the IQE of the LaSiO$_2$N:0.06Eu prepared at 1500 °C, 1525 °C and 1550 °C were estimated to be about 3.48%, 12.48% and 20.01%, respectively, under 365 nm excitation. The enhanced IQE matched well with the variation trend of emission intensity. Although the IQE of LaSiO$_2$N:0.06Eu is lower than that of commercial YAG (61%)$^{42}$, it can be further improved by optimization of the preparation conditions, because the QE depends closely on the prepared conditions, crystalline defects, particle size and morphology of the phosphor$^{43,44}$.

In order to well understand the luminescent performance of this phosphor, the temperature-dependent luminescent properties of LaSiO$_2$N:0.06Eu phosphor was measured during the temperature ranges of 25–200 °C. As presented in Fig. 11a, the emission intensity decreased with increasing temperature. At 100 °C and 150 °C, the PL intensity quenched to 62.8% and 42.3%. The thermal quenching effect of this phosphor is more intense than...
the commercial YAG:Ce clusters, while similar to La–Si–O–N system phosphors. The thermal quenching can be explained by the model of thermal excitation of the 5d electron to conduction band states. When Eu2+ substituted in a trivalent site, the Eu2+ had the trend to be ionized to Eu3+, which reduced the activation energy and lead to stronger thermal quenching. To determine the activation energy for thermal quenching, the Arrhenius equation was used to estimate the thermal quenching:

$$\ln\left(\frac{I_0}{I}\right) = \ln A - \frac{\Delta E}{kT}$$

where $I_0$ and $I$ mean the luminescence intensity of LaSiO2N:Eu at room temperature and a given temperature, respectively; $A$ is a constant; $k$ presents the Boltzmann constant ($8.617 \times 10^{-5}$ eV K$^{-1}$). Figure 11b plots $\ln((I_0/I)-1)$ variation dependence of $1/(kT)$, and the $\Delta E$ was calculated to be about 0.24 eV.

To further assess the potential application of the LaSiO2N: Eu phosphors, the yellow emitting LaSiO2N:0.01Eu phosphor prepared at 1500 °C and LaSiO2N:0.06Eu phosphors prepared at 1550 °C were mixed with blue-emitting BAM: Eu2+ phosphor, respectively, and then the mixtures were severally combined with a 385 nm NUV chip to fabricate white LED lamps. The electroluminescent (EL) spectra of these lamps driven by 30 mA current were depicted in Fig. 12. The CIE color coordinates, CCT and CRI of the fabricated W-LED lamp with LaSiO2N:0.01Eu phosphor prepared at 1500 °C were determined to be (0.32, 0.38), 5959 and 76, respectively (Figure S3 and Fig. 12a). Via utilizing the redshift, varied valence and efficient energy transfer, the fabricated W-LED lamp with the red region enhanced yellow-emitting LaSiO2N:0.06Eu phosphor displayed an entire white spectrum with a CIE color coordinates of (0.33, 0.36), a CCT of 5783 K and a CRI of 87 (Figure S3 and Fig. 12b). Compared with the W-LED lamp using commercial YAG:Ce phosphor in previous study (CIE = 0.302, 0.315; CCT = 7272 K, Ra = 78.38), the CCT of as-fabricated LEDs was relative low and the Ra was high, suggesting that the high CRI warm W-LEDs could be easily obtained by altering the concentration of doping ions and the preparation temperature.

Conclusions

In summary, a novel Eu-activated LaSiO2N yellow-emitting phosphor has been synthesized and evaluated for the application in W-LEDs. With the aid of crystal structure, valence-varied, redshift, and energy transfer, the red region enhanced yellow-emitting LaSiO2N Eu phosphor has been designed and realized by controlling the concentration of doping ions and the preparation temperature. A high CRI and warm W-LED lamp was obtained in combination with this phosphor, proving that the red region enhanced LaSiO2N Eu phosphor has a great
potential for the application in W-LEDs. More importantly, this study would provide a new strategy for designing Eu-activated yellow-emitting phosphors by synergistically enhancing the red region and emission intensity to adjust the CCT and CRI for warm W-LEDs application without reducing the other luminescence properties.

**Methods**

**Materials and Synthesis.** The LaSiO2N:Eu was synthesized from stoichiometric mixtures of La2O3 (analytical reagent (A. R.)), α-Si3N4 (A. R.) and Eu2O3 (A. R.). The ground powders were placed in alumina crucibles and fired for 6 h in a reducing atmosphere (10% H2 + 90% N2) at 1500 °C, 1525 °C and 1550 °C, respectively. Then, the precursor was reground and heated again at same condition. Thereafter, the samples were cooled down to room temperature naturally and powdered for subsequent analysis.

**Materials Characterization.** Powder X-ray diffraction on a D8 Advance diffractometer (Germany) with graphite-monochromatized Cu Kα radiation (λ = 0.154 06 nm) was recorded for the structure of all samples. Photoluminescence spectra were collected using a Hitachi F-4600 fluorescence spectrophotometer (Japan) equipped with a 150 W Xe lamp as the excitation source. Diffuse reflection spectra were recorded using a Shimadzu UV-3600 UV−vis−NIR spectrophotometer attached with an integrating sphere. BaSO4 was used as a reference for 100% reflectance. The morphology was observed using scanning electron microscopy (SEM; JSM-6460LV, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed in a PHI 5300 ESCA system using an Al Kα X-ray source with constant pass energy of 55.00 eV. The charge effect referred to the C1s signal (284.6 eV). The room-temperature luminescence decay curves were obtained from a spectrofluorometer (Horiba, Jobin Yvon) using a tunable pulse laser radiation (nano-LED) as the excitation. Quantum efficiency was measured by a fluoromax-4 spectrofluorometer (Horiba, Jobin Yvon) with an integral sphere at room temperature.

**References**

1. Lu, W., Jia, Y., Zhao, Q., Lv, W. & You, H. Design of a luminescence pattern via altering the crystal structure and doping ions to create warm white LEDs. *Chem. Commun.*, 50, 2635–2637 (2014).
2. Pust, P. et al. Ca[LiAl3N4]: Eu2+ A Narrow-Band Red-Emitting Nitridolithooaluminate. *Chem. Mater.* 26, 3544–3549 (2014).
3. Yeh, C.-W. et al. Origin of Thermal Degradation of Sr2−xSi5N8:Eux Phosphors in Air for Light-Emitting Diodes. *J. Am. Chem. Soc.* 134, 14108–14117 (2012).
4. Huang, C.-H., Chiu, Y.-C., Yeh, Y.-T., Chan, T.-S. & Chen, T.-M. Eu2+-Activated Sr2ZnSc(P2O7)2: A Novel Near-Ultraviolet Converting Yellow-Emitting Phosphor for White Light-Emitting Diodes. *ACS. Appl. Mater. Inter.* 4, 6661–6668 (2012).
5. Zhang, X., Fei, L., Shi, J. & Gong, M. Eu2+-Activated Eu activator. *Physica B: Condensed Matter* 406, 2616–2620 (2011).
6. Wu, Z., Gong, M., Shi, J., Wang, G. & Su, Q. Dibarium magnesium diphosphate yellow phosphor applied in InGaN-based LEDs. *Chem. Lett.* 36, 410–411 (2007).
7. Jang, H. S., Kim, Y.-S., Kim, Y.-S. & Lee, H. S. & Jeon, D. Y. Yellow-emitting γ-Si3N4: Ce3+, Li+ phosphor for solid-state lighting: luminescent properties, electronic structure, and white light-emitting diode application. *Opt. Express* 20, 2761–2771 (2012).
8. Song, W.-S., Kim, Y.-S. & Yang, H. Yellow-emitting phosphor of Sr18O14Eu2+: Eu2+ for application to white-light-emitting diodes. *Mater. Chem. Phys.* 117, 500–503 (2009).
9. Jang, H. S. & Jeon, D. Y. White light emission from blue and near ultraviolet light-emitting diodes precoated with a Sr3SiO7:Ce3+, Li+ phosphor. *Opt. Lett.* 32, 3444–3446 (2007).
Author Contributions

Y.L. and J.C. conceived the project. J.C. and L.M. designed and performed the experiments. J.C., P.P. and H.L. analyzed the data. J.C. and Q.C. wrote the manuscript. All the authors discussed the results and commented on the manuscript at all stages.
Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Chen, J. et al. Design of a Yellow-Emitting Phosphor with Enhanced Red Emission via Valence State-control for Warm White LEDs Application. Sci. Rep. 6, 31199; doi: 10.1038/srep31199 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/

© The Author(s) 2016