

Strategy to optimize the broadband near-infrared emission based on Eu²⁺-doped sulfured garnet phosphors toward emerging spectroscopy applications

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Abstract

Eu²⁺-doped near-infrared (NIR) emitting phosphors, known for their high efficiency, broadband emission and spectral tunability, have gained much attention. However, achieving efficient NIR emission based on Eu²⁺ remains a challenge due to the co-existence of Eu³⁺, especially in materials (i.e. garnets and apatites) containing trivalent lanthanide cations. In this study, a Eu²⁺ doped sulfured NIR-emitting garnet phosphor Ca₃(Sc, Eu)₂Si₃(O, S)₁₂: Eu²⁺ is successfully designed and synthesized. Notably, a strategy for regulating the initial valence state of dopants is proposed by using prepared EuS instead of the conventional Eu₂O₃ as raw material, enhancing the NIR emission by 135%. Moreover, a sulfuration strategy is further introduced to enhance the NIR-emitting intensity and internal quantum efficiency by 192% and 167.8%, and to improve thermal stability by 154% at 120°C. The luminescence origin of the unusual broadband NIR emission is re-examined through chemical unit co-substitution strategy by introducing [Al³⁺-Hf⁴⁺] to replace [Sc³⁺-Si⁴⁺] ion pairs. Meanwhile, the spectral regulation and the performance optimization mechanism are systematically discussed. Finally, a green light pumped NIR LED device with a photoelectric efficiency of 9.43%@100 mA and output power of 22.74 mW@100 mA is fabricated, showing remarkable potential in nondestructive testing and biomedical imaging applications.

Keywords: Garnet structure; Eu²⁺; sulfuration strategy; Broadband NIR emission; pc-NIR LED.

1. Introduction

NIR spectroscopy technique is widely used in nondestructive testing, biomedical imaging, medical diagnosis and food quality assessment due to its advantages of being nondestructive,

rapid and cost-effective, etc.[1-3] Among the components of NIR spectroscopy system, NIR light sources are crucial. They need to be compact and have high energy efficiency to meet the requirements of NIR spectroscopy applications.[4] However, the ability of traditional NIR light sources (such as tungsten filament and halogen lamps) to be easily combined with smartphones or portable devices for various fast and convenient applications has been limited by their low efficiency and large size.[5] Recently, researchers have proposed a portable phosphor-converted NIR LED (pc-NIR LED) inspired by the commercially white LED technology. This device is based on a blue LED chip (450 ~ 470 nm) coating on a broadband NIR-emitting phosphor, effectively solving the above disadvantages.[6, 7] However, as a non-visual light-source, pc-NIR LED may not require a blue LED chip as a necessary component, due to drawbacks such as the large Stokes shift and the leakage of blue light.[8] To acquire a pc-NIR LED with high efficiency and human eye security, green light pumped pc-NIR LED could be a viable alternative. Unfortunately, there are few reports have reported on the work of NIR-emitting phosphors based on green LED chips.[9]

Currently, the activator ions achieving efficient NIR emission are mainly Cr^{3+} and Eu^{2+} . However, the broadband NIR emission of Cr^{3+} requires a weak crystal field environment ($Dq/B < 2.3$).[10] In addition, the Cr^{3+} shows strong absorption in ultraviolet (UV) and blue regions but weak absorption in green region based on its $^4A_2 \rightarrow ^4T_1$ transition.[11, 12] In contrast, the 5d orbital of Eu^{2+} is exposed in the outer layer, resulting in its absorption and luminescence are easily affected by the surrounding crystal field environment, that is, the absorption can cover the ultraviolet-visible region and produce efficient visible-NIR emission.[13-17] Recently,

several Eu^{2+} doped NIR-emitting phosphors with excellent optical properties have been reported, such as $\text{Ba}_3\text{ScB}_3\text{O}_9: \text{Eu}^{2+}$ ($\lambda_{\text{ex}} \approx 376 \text{ nm}$, $\lambda_{\text{em}} \approx 735 \text{ nm}$), $\text{SrBaSc}_{0.5}\text{Ga}_{1.5}\text{O}_5: \text{Eu}^{2+}$ ($\lambda_{\text{ex}} \approx 440 \text{ nm}$, $\lambda_{\text{em}} \approx 728 \text{ nm}$), $\text{Ba}_3\text{Lu}(\text{BO}_3)_3: \text{Eu}^{2+}$ ($\lambda_{\text{ex}} \approx 450 \text{ nm}$, $\lambda_{\text{em}} \approx 720 \text{ nm}$) and $\text{CaO}: \text{Eu}^{2+}$ ($\lambda_{\text{ex}} \approx 470 \text{ nm}$, $\lambda_{\text{em}} \approx 740 \text{ nm}$). [18-21] It is evident that the NIR emission of Eu^{2+} typically lies in the deep red region, and the Eu^{2+} doped luminescent materials with long-wavelength NIR emission are rarely reported. However, long-wavelength NIR luminescence is crucial for emerging NIR spectroscopy applications, such as vein imaging ($\sim 780 \text{ nm}$), corneal recognition ($\sim 810 \text{ nm}$), night vision ($\sim 850 \text{ nm}$), food detection ($\sim 970 \text{ nm}$), and long-wavelength fluorescent probes (1000-1700 nm). [22] Therefore, there is an urgent need to develop Eu^{2+} doped long-wavelength NIR-emitting phosphors to satisfy the multi-functional application demands of the emerging NIR spectroscopy applications.

Berezovskaya et al. were the first to report an unusual long-wavelength NIR emission phenomenon of a silicate garnet phosphor $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}: \text{Eu}^{2+}$ (CSSO: Eu^{2+} , only the excitation and emission spectra were reported). [23] Furthermore, Berezovskaya mentioned that the emission of incompletely reduced Eu^{3+} was observed under 520 nm excitation. Later, Zhou et al. investigated the luminescence and energy transfer process from Ce to Eu to improve the energy conversion efficiency in solar cells. [24] However, the detail luminescence origin of the unusual broadband NIR emission, the strategy to stabilize the valence state of Eu^{2+} and the emerging NIR spectroscopy application have not been verified or reported. In fact, the co-existence of Eu^{3+} has become a troublesome problem in many Eu^{2+} doped phosphors, especially in those containing trivalent lanthanide cations, such as in garnet and apatite-type

phosphors.[25-28] Therefore, exploring effective strategies to stabilize the valence state of Eu^{2+} and enhance its NIR luminescence properties in Eu^{2+} doped phosphors is urgent.

In this work, we successfully designed and synthesized a series of Eu^{2+} doped NIR-emitting sulfureted garnet phosphors $\text{Ca}_3(\text{Sc}, \text{Eu})_2\text{Si}_3(\text{O}, \text{S})_{12}:\text{Eu}^{2+}$ (CSSO: Eu^{2+} , S^{2-}), and conducted an in-depth study on their phase component and characteristic properties of NIR spectroscopy. In addition, we used a chemical unit co-substitution strategy to modify the local structure of Sc^{3+} ions in CSSO: Eu^{2+} , and determined the luminescence origin of the unusual broadband NIR emission. Above all, we proposed a strategy for regulating the initial valence state of dopants by using the prepared EuS (Eu valence state is divalent) instead of the conventional Eu_2O_3 (Eu valence state is trivalent) as raw material, effectively reducing the Eu^{3+} content and achieving a significant enhancement in the NIR emission intensity. Furthermore, we proposed a sulfurization strategy to further enhance the NIR emission intensity and improve the thermal stability. Finally, an efficient pc-NIR LED is prepared by combining a 520 nm green chip with the optimum sample, and the potential application of the above pc-NIR LED on nondestructive testing and biomedical imaging was demonstrated.

2. Results and discussion

2.1 Crystal structure, phase purity and morphological analysis of CSSO: Eu^{2+} and CSSO: Eu^{2+} , S^{2-} samples.

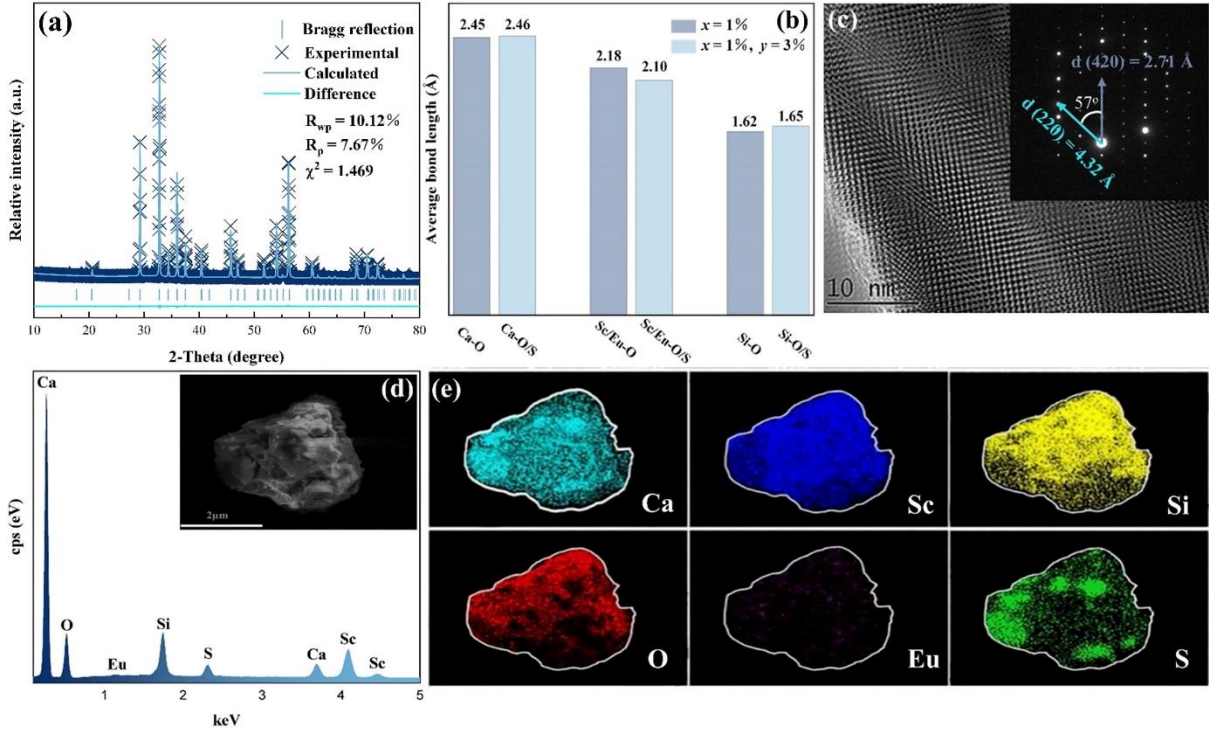


Figure 1(a) Rietveld refinement of CSSO: 1% Eu^{2+} , 3% S^{2-} sample; (b) The average bond length distributions histograms of the CSSO: 1% Eu^{2+} and CSSO: 1% Eu^{2+} , S^{2-} samples; (c) HRTEM and SAED image of CSSO: 1% Eu^{2+} , 3% S^{2-} sample; (d) and (e) EDS spectra and elemental mapping of a single CSSO: 1% Eu^{2+} , 3% S^{2-} sample particle.

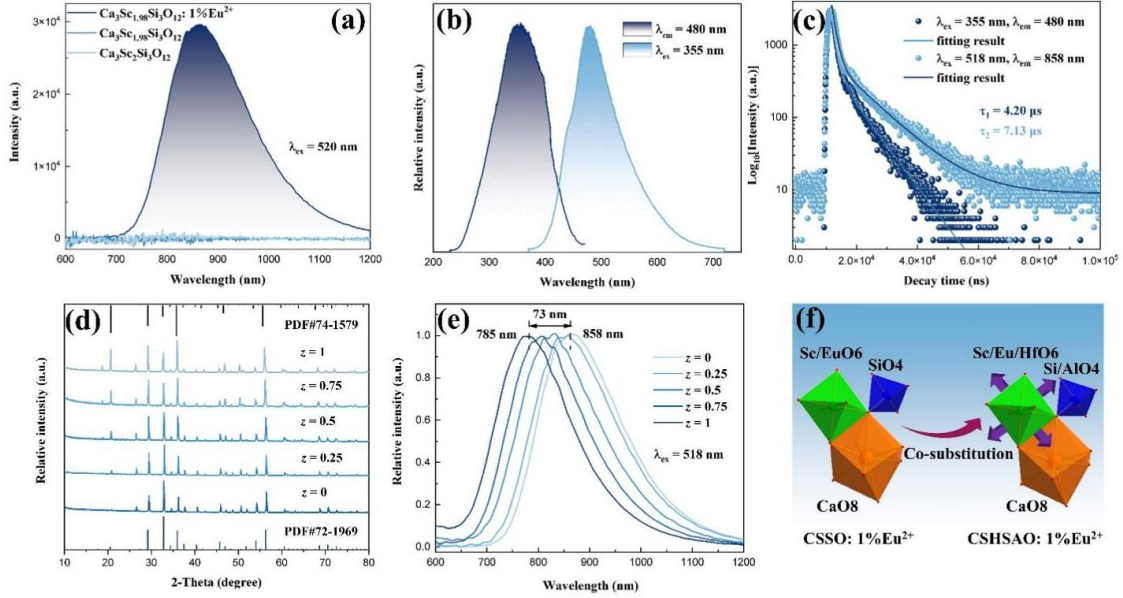
The XRD diffraction patterns of prepared EuS and samples with different Eu^{2+} and S^{2-} concentrations are shown in Fig. S1-S3, indicating that the prepared EuS is single phase. Furthermore, the XRD patterns of CSSO: $x\text{Eu}^{2+}$, $y\text{S}^{2-}$ ($0 \leq x \leq 5\%$, $0 \leq y \leq 7\%$) samples are consistent with that of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ (PDF#72-1969), implying that all samples are pure phases. In order to compare the changes in crystal structure information between the CSSO: 1% Eu^{2+} and CSSO: 1% Eu^{2+} , 1% S^{2-} samples, Rietveld refinement analysis is performed on the XRD diffraction patterns within the 2θ range from 10° to 80° using GSAS software, and the

refinement results are shown in Fig. 1a, S4 and Table S1-S6. The refinement results show that CSSO: 1%Eu²⁺ and CSSO: 1%Eu²⁺, 3%S²⁻ samples have cubic structure with an Ia-3d (230) space group. It is worth noting that with the addition of S, the unit cell parameter *a* increases from 12.21 Å to 12.25, and *V* expands from 1820.32 Å³ to 1838.26 Å³, which is due to the substitution of larger S²⁻ for smaller O²⁻. [29] Additionally, the [Ca-O/S] bond length remains unchanged, the [Si-O/S] bond length slightly increases, and the [Sc/Eu-O/S] bond length becomes shorter, as shown in Fig. 1b. Consequently, the contraction of [Sc/Eu-O/S]₆ octahedron will lead to the increase of the crystal field strength around Eu²⁺ and further cause a red shift of the photoluminescence spectrum, which will be discussed later.

Figures S5 and S6 show the SEM images of CSSO: 1%Eu²⁺ and CSSO: 1%Eu²⁺, 3%S²⁻ samples and the tendency to form agglomerates can be observed, which results from the rapid aggregation of the samples during high-temperature sintering. [30] Furthermore, with the doping of S²⁻, the surface morphology of the particles transitions from sharp to smooth, and the average grain size increases from 34.01 to 51.56 μm. These changes indicate that the doping of S²⁻ has a fluxing effect and can improve the crystallinity of the phosphor. [31, 32] In addition, the high crystallinity of the sample is further confirmed by the clear lattice stripes in the HRTEM image, as shown in Fig. 1c. At the same time, the selected area electron diffraction pattern clearly presents the *d*(220) = 4.32 Å and *d*(420) = 2.71 Å planes of the garnet structure, [33] which also demonstrates the successful synthesis of the targeted phosphors. Meanwhile, the distribution of Ca, Sc, Si, O, Eu and S in the whole particle can be observed from the elemental mapping images of a single sample particle, which further confirms that S

1 has been successfully doped into CSSO: 1%Eu²⁺, 3%S²⁻, as shown in Fig. 1d and 1e.

2 2.2 The luminescence origin of the NIR emission in Eu²⁺ doped CSSO: Eu²⁺ sample.



3
4 Figure 2(a) The emission spectra of CSSO: 1%Eu²⁺, Ca₃Sc_{1.98}Si₃O₁₂ and CSSO samples under 518 nm
5 excitation; (b) The excitation and emission spectra of CSSO: 1%Eu²⁺ sample under the $\lambda_{ex} = 355$ nm and
6 $\lambda_{em} = 480$ nm; (c) The decay time of different wavelengths for CSSO: 1%Eu²⁺ sample; (d) The XRD
7 patterns of Ca₃Sc_{1.98-z}Hf_zSi_{3-z}Al_zO₁₂: 1%Eu²⁺ ($0 \leq z \leq 1$) samples; (e) The normalized emission spectra of
8 Ca₃Sc_{1.98-z}Hf_zSi_{3-z}Al_zO₁₂: 1%Eu²⁺ ($0 \leq z \leq 1$) samples; (f) The expansion mechanism of the EuO₆
9 polyhedron with [Al³⁺-Hf⁴⁺] substituted for [Sc³⁺-Si⁴⁺] ion pairs.

10 Berezovskaya and Zhou et al. mentioned that the unusual broadband NIR emission in
11 CSSO: Eu²⁺ likely originates from Eu²⁺ ions occupying the octa-coordinated Ca²⁺ sites.[23, 24]
12 However, in some other Eu²⁺ doped garnet-type phosphor, reports indicate that if Eu²⁺ occupy
13 the octa-coordinated sites with weak crystal field strength, blue or cyan emission will be
14 obtained, resulting from the 5d→4f transitions of Eu²⁺, such as in Lu₂CaMg₂Si₃O₁₂: Eu²⁺ (λ_{ex}
15 ≈ 365 nm, $\lambda_{em} \approx 450$ nm), Lu₂MgAl₄SiO₁₂: Eu²⁺ ($\lambda_{ex} \approx 365$ nm, $\lambda_{em} \approx 463$ nm) and Ba₃Y₂Si₃O₁₂:
16 Eu²⁺ ($\lambda_{ex} \approx 365$ nm, $\lambda_{em} \approx 505$ nm).[34-36] Recently, Xia et al. demonstrated that short bond
17 lengths around the six-coordinated Eu²⁺ could contribute to its NIR emission, although Eu²⁺
18 occupy an inequivalent Y³⁺ sites in (Sr, Ba)Y₂O₄: Eu²⁺. [37] Additionally, oxygen vacancies are

demonstrated to be able to generate a broadband NIR emission.[38] Thus, it is necessary to re-examine the luminescence origin of the unusual broadband NIR emission in CSSO: Eu²⁺. First, considering the reductive atmosphere during the sintering process and the possible inequivalent substitution when Eu²⁺ enter Sc³⁺ sites (as described by defect equation S1). It is necessary to determine that whether the unusual broadband NIR emission originates from the oxygen vacancies. Therefore, the Sc³⁺ absent sample Ca₃Sc_{1.98}Si₃O₁₂ is successfully synthesized (Fig. S7) and the emission spectra of Ca₃Sc_{1.98}Si₃O₁₂, CSSO and CSSO: 1%Eu²⁺ samples prepared in a reductive atmosphere are measured under 518 nm excitation, as shown in Fig. 2a. However, the Ca₃Sc_{1.98}Si₃O₁₂ and CSSO samples do not exhibit any visible or NIR emission, which confirms that the unusual broadband NIR emission in CSSO: Eu²⁺ should not be related to the oxygen vacancies luminescence but stem from the 5d→4f transition of Eu²⁺.

Moreover, it is worth noting that a blue emission band centered at 480 nm is observed under 355 nm excitation (Fig. 2b) for CSSO: 1%Eu²⁺ sample, which is not mentioned in Berezovskaya and Zhou's report.[23, 24] Regarding this, we hypothesize that the blue emission should be attributed to the substitution of Eu²⁺ for the octa-coordinated Ca²⁺ ions, as reported in Eu²⁺ doped other garnet systems, [34-36] while the latter broadband NIR emission should due to the substitution of Eu²⁺ for the six-coordinated Sc³⁺ ions. To further confirm the above hypothesis and determine the relation between the site occupation and luminescence characteristic, we compared the crystal field strength (ϵ_{CFS}) around Eu²⁺ using the following equation,[37]

$$\epsilon_{\text{CFS}} = \beta_{\text{poly}}^{\text{Q}} R_{\text{av}}^{-2} \quad (1)$$

$$R_{av} = \frac{1}{n} \sum_{i=1}^{CN} (R_i - 0.6(R_M - R_{Ln})) \quad (2)$$

Where Q is 2+ for Eu^{2+} ; β_{poly}^Q is a constant; R_i is the individual bond length to the CN coordinating anions in the unrelaxed lattice; R_M is the cationic radius and R_{Ln} is the ionic radius of lanthanide. According to the formulas (1,2), it can be found that ϵ_{CFS} is negatively correlated with R_{av} , that is, Eu^{2+} occupy cationic sites with a small coordination number, which enhances ϵ_{CFS} and reduces the energy of the 5d excited state.[39] In this work, the R_{av} value of Sc^{3+} (~ 2.44 Å) is smaller than that of Ca^{2+} (~ 2.52 Å). Therefore, the emission peak located in the blue region (~ 480 nm) is attributed to the Eu^{2+} occupying the Ca^{2+} site, while the emission peak located in the NIR region (~ 858 nm) is attributed to the Eu^{2+} occupying the Sc^{3+} site. The decay time of the CSSO: 1% Eu^{2+} sample monitored at 480 and 858 nm is measured to be 4.20 and 7.13 μs , as shown in Fig. 2c and Table S7, which further supports that the blue and NIR emissions in CSSO: 1% Eu^{2+} sample are attributed to the 5d $\rightarrow$ 4f transition of Eu^{2+} occupying two different luminescence centers, respectively.

Furthermore, considering that the emission of Eu^{2+} is quite sensitive to the crystal field strength, we utilized a chemical unit co-substitution strategy to regulate the lattice environment around the Sc^{3+} site by replacing [Sc^{3+} - Si^{4+}] with [Al^{3+} - Hf^{4+}] ion pairs, and then design and successfully synthesized a series of new solid solution phosphors $Ca_3Sc_{1.98-z}Hf_zSi_{3-z}Al_zO_{12}$: 1% Eu^{2+} ($0 \leq z \leq 1$) samples, as confirmed by XRD analysis in Fig. 2d. It is worth mentioning that a significant preferred orientation occurs with increasing [Al^{3+} - Hf^{4+}] doping concentration, and the XRD pattern of the $Ca_3Sc_{0.98}HfSi_2AlO_{12}$: 1% Eu^{2+} ($z = 1$) sample is consistent with the standard card of the garnet-structured compound $Ca_3In_2Si_3O_{12}$ (PDF#74-1579). Notably, due to

the large ion radius of Al^{3+} and Hf^{4+} , the mean peak at 36 degree (2θ) is found to slightly shift toward the small angle direction, as shown in Fig. S8. This shift indicates the successful replacement of $[\text{Al}^{3+}\text{-Hf}^{4+}]$ ion pairs by $[\text{Sc}^{3+}\text{-Si}^{4+}]$. The normalized excitation and emission spectra of $\text{Ca}_3\text{Sc}_{1.98-z}\text{Hf}_z\text{Si}_{3-z}\text{Al}_z\text{O}_{12} : 1\%\text{Eu}^{2+}$ ($0 \leq z \leq 1$) samples are recorded in Fig. S9 and 2e. As expected, the emission spectra are largely blue shifted from 858 to 785 nm, and the corresponding excitation spectra shifts from 518 to 470 nm. This shift can be assigned to the inhibited the splitting of the 5d energy level of Eu^{2+} due to the decrease of the crystal field strength after the replacement of $[\text{Sc}^{3+}\text{-Si}^{4+}]$ with larger $[\text{Al}^{3+}\text{-Hf}^{4+}]$ ion pairs as shown in Fig. 2f.[29, 40] The above results further support that the unusual broadband NIR emission in CSSO: 1% Eu^{2+} sample should stem from the 5d $\rightarrow$ 4f transitions of Eu^{2+} occupying the six-coordinated Sc^{3+} sites.

2.3 Stabilization of Eu^{2+} ions and luminescence enhancement investigation through EuS doping.

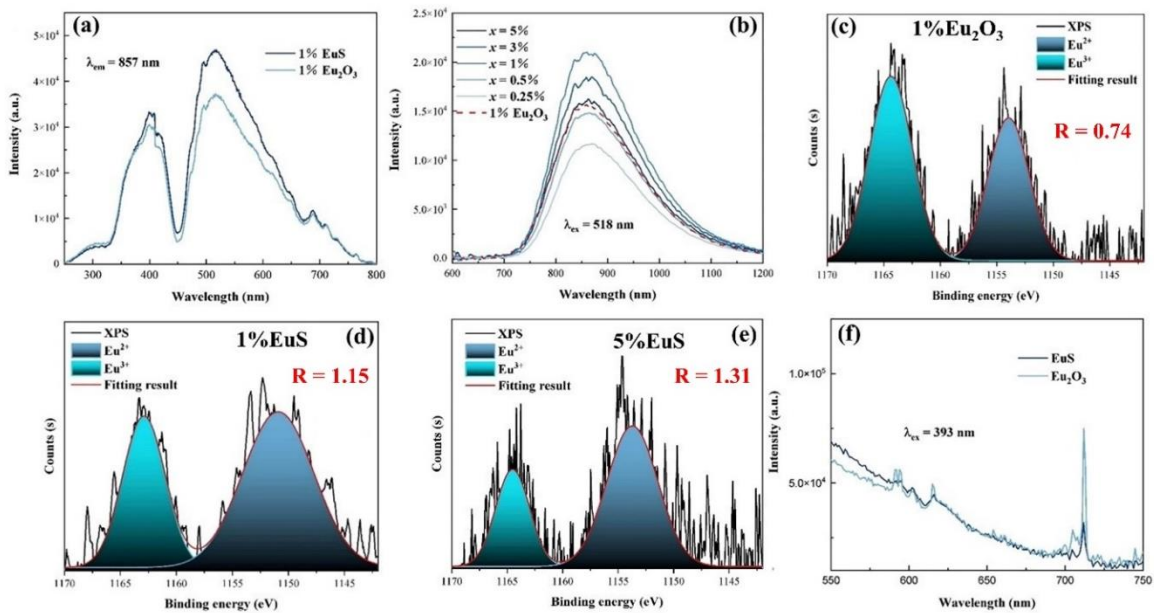


Figure 3(a) The excitation spectra of CSSO: 1% Eu^{2+} sample with EuS and Eu_2O_3 as raw material; (b) The emission spectra of CSSO: $x\text{Eu}^{2+}$ ($0.25\% \leq x \leq 5\%$) and CSSO: 1% Eu^{2+} samples with Eu_2O_3 as raw

material; (c)-(e) XPS spectra of the Eu 3d_{3/2} level from samples prepared with varying Eu raw materials and EuS concentrations; (f) The emission spectra of CSSO: 1%Eu²⁺ sample under 393 nm excitation with different Eu raw materials.

Due to the inequivalent substitution in CSSO: Eu²⁺, stabilizing the valence state of Eu²⁺ is crucial. Although some methods have been used in the previous works, such as carbothermal reaction method, additional annealing in a reducing atmosphere, adding additional ZnO as a compensating agent or controlling the reaction temperature,[23, 41-43] but the results are not satisfactory and universal. In this work, we proposed a strategy to control the initial valence state of the dopant by using the prepared EuS (Eu valence state is divalent) instead of conventional Eu₂O₃ (Eu valence state is trivalent) as the raw material, and the comparison of their excitation and emission spectra are illustrated in Fig. 3a and 3b. It is obvious that the spectra are almost the same except for the intensity, that is, the spectra intensity of EuS doped sample can be increased by about 135% than that of using Eu₂O₃ as a raw material. The optimal doping content of EuS in CSSO is then determined to be 1%.

To clarify the luminescence optimization mechanism, the XPS spectra on the Eu 3d_{3/2} levels of 1% Eu₂O₃ and 1% EuS samples are measured, as shown in Fig. 3c and 3d. Excitingly, the XPS signal intensity ratio R of Eu²⁺ and Eu³⁺ in the EuS-doped sample is determined to be 1.15, which is much higher than that of the Eu₂O₃-doped sample (R = 0.74). Furthermore, in order to avoid the error caused by the low concentration doping of EuS, we also specially performed XPS tests on the sample doped with high concentrations of EuS, as shown in Fig. 3e. The results indicate that high-concentration doping of EuS can also significantly enhance the R value of the sample (R = 1.31). This demonstrates that Eu²⁺ can be effectively stabilized through the proposed strategy by the regulating initial valence state of the dopant.[14, 42, 44,

45] The above inference can also be further demonstrated by utilizing the selective excitation characteristics of Eu^{3+} ions. To address this, the emission spectral of the above two samples under 393 nm excitation (the characteristic excitation wavelength of Eu^{3+} ions) are shown in Fig. 3f. For the sample doped with the prepared EuS, the emission spectra show weaker line-sharp emissions peaked at 594, 615, 653 and 711 nm, corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_i$ ($i = 1, 2, 3, 4$) transitions of Eu^{3+} , [41, 46] further indicating that more Eu^{2+} can be stabilized at high temperatures by using EuS as raw material. This stabilization is beneficial for enhancing the NIR-emitting intensity of Eu^{2+} .

2.4 Enhanced NIR emission analysis through sulfuration strategy.

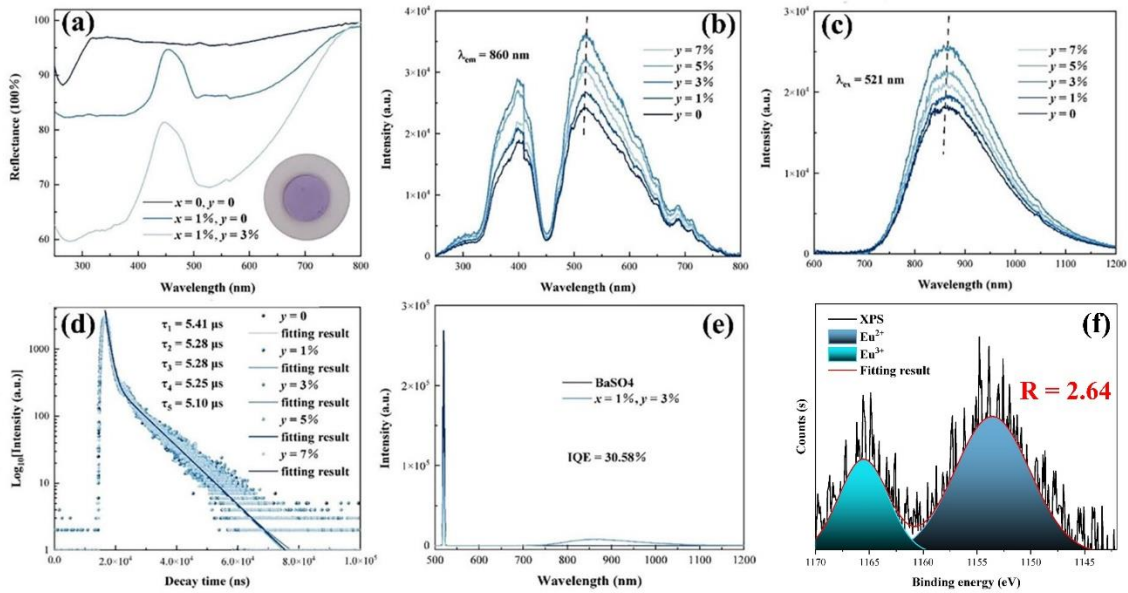


Figure 4(a) DRS spectra of CSSO, CSSO: 1% Eu^{2+} and CSSO: 1% Eu^{2+} , 3% S^{2-} samples, the inset shows digital photo of the CSSO: 1% Eu^{2+} , 3% S^{2-} sample; (b) and (c) The excitation and emission spectra of CSSO: 1% Eu^{2+} , $y\text{S}^{2-}$ ($0 \leq y \leq 7\%$) samples; (d) The decay curves of CSSO: 1% Eu^{2+} , $y\text{S}^{2-}$ ($0 \leq y \leq 7\%$) samples; (e) The internal quantum efficiency of CSSO: 1% Eu^{2+} , 3% S^{2-} sample; (f) XPS spectra of the Eu $3d_{3/2}$ level of CSSO: 1% Eu^{2+} , 3% S^{2-} sample.

To further optimize the NIR luminescence behavior, we proposed a sulfuration strategy by co-doping S^{2-} into CSSO: 1% Eu^{2+} sample. The diffuse reflection spectra (DRS) of the CSSO, CSSO: 1% Eu^{2+} and CSSO: 1% Eu^{2+} , 3% S^{2-} samples are shown in Fig. 4a. The spectra contain

two strong absorbance bands in 250-800 nm region with maxima at around 400 and 520 nm, attributed to the 5d→4f transition of the Eu^{2+} . Notably, the S^{2-} doping significantly enhances the phosphor absorption in the corresponding region. The inset of Fig 4a and S10 are digital photos of the CSSO: 1% Eu^{2+} , 3% S^{2-} and CSSO samples, respectively. The Eu^{2+} doped sample show an attractive purple color, consistent with its strong absorption in the violet and green light region. The excitation and emission intensity are gradually enhanced with increasing S^{2-} doping content, as shown in Fig. 4b and 4c. When the doping content of S^{2-} reaches 3%, the emission intensity of CSSO: 1% Eu^{2+} , 3% S^{2-} sample is enhanced to 192% compared to that of CSSO: 1% Eu^{2+} sample using Eu_2O_3 as raw material. Furthermore, both the excitation and emission spectra exhibit slight red shifts, attributed to the contraction of the $[\text{Sc}/\text{Eu}-\text{O}/\text{S}]_6$ octahedron that enhances the crystal field strength around Eu^{2+} , resulting in an increase in crystal field splitting.[37] Meanwhile, the larger electron cloud expansion effect caused by the smaller electronegativity of S^{2-} (2.45) compared to O^{2-} (3.44),[47, 48] leads to a decrease in the 5d orbital, which also contributes to the red shifts in both spectra. This further confirms the successful doping of S^{2-} into the sample. Fig. 4d and Table S8 illustrate the decay curves of CSSO: 1% Eu^{2+} , $y\text{S}^{2-}$ ($0 \leq y \leq 7\%$) samples excited at 521 nm and monitored at 860 nm. The microsecond order of the lifetime is consistent with that of Eu^{2+} doped NIR-emitting phosphors.[20, 49] In addition, the lifetime shows a slight decrease along with increasing S^{2-} content, implying that the doping of S^{2-} has a small effect on the probability of radiative energy transition involving Eu^{2+} ions.

Excitingly, the internal quantum efficiency (IQE) of the CSSO: 1% Eu^{2+} , 3% S^{2-} sample

reaches 30.58%, marking a staggering 167.8% enhancement in quantum efficiency compared to the CSSO: 1%Eu²⁺ sample prepared using Eu₂O₃ as the raw material (IQE = 18.22%), as shown in Fig. 4e and S11. In order to further verify and reveal the luminescence enhancement mechanism, the XPS spectra on the Eu 3d_{3/2} levels of CSSO: 1%Eu²⁺, 3%S²⁻ sample is measured as shown in Fig. 4f. The R value of Eu²⁺ and Eu³⁺ in the EuS and S²⁻ co-doped sample is determined to be 2.64, which is much higher than that of the Eu₂O₃-doped sample (R = 0.74). This is because the addition of S²⁻ can promote the spontaneous transformation of Eu³⁺ to Eu²⁺,[50] thereby increasing the R value and enhancing the luminescence intensity. Additionally, the improvement in crystallinity and absorption due to sulfuration also enhances the luminescence intensity and quantum efficiency, as supported by SEM and DRS analysis (Fig. S5, S6 and 4a).

2.5 The thermal stability property investigation of CSSO: Eu²⁺ and CSSO: Eu²⁺, S²⁻ samples.

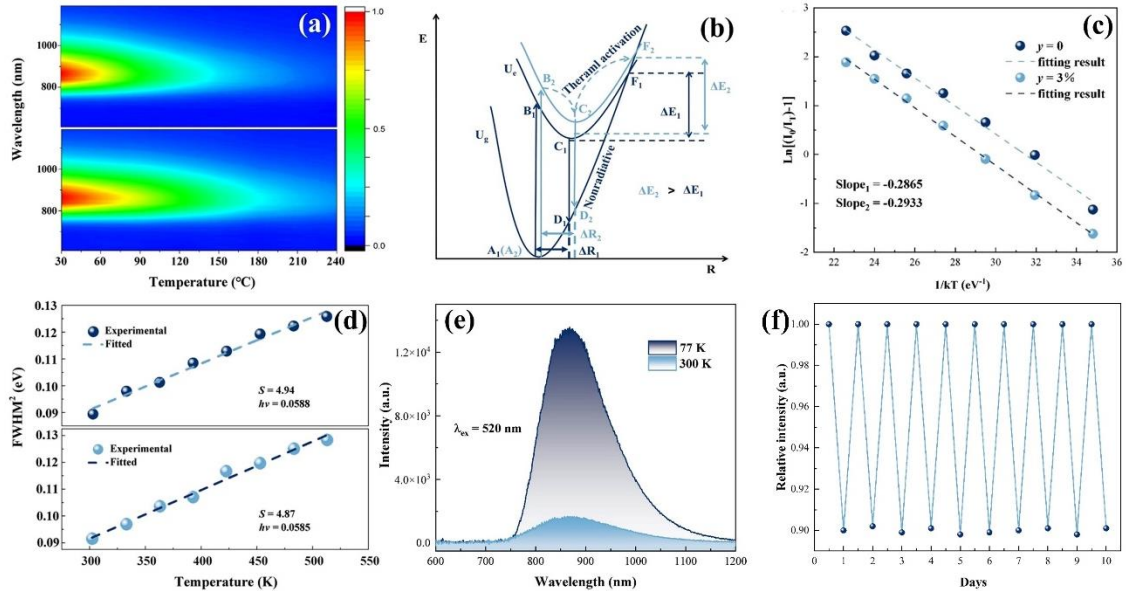


Figure 5(a) Contour plot of the temperature-dependent emission spectra; (b) The configuration coordinate diagram of thermal quenching; (c) and (d) The relationship of $\ln[(I_0/I_T)-1]$ with $1/kT$, Huang-Rhys factor and phonon energy of CSSO: 1%Eu²⁺ and CSSO: 1%Eu²⁺, 3%S²⁻ samples; (e) Emission spectra of CSSO: 1%Eu²⁺, 3%S²⁻ sample at 77K and 300K; (f) The relative luminous intensity of CSSO: 1%Eu²⁺, 3%S²⁻ sample in humid environment for ten days.

The temperature-dependent emission spectra of the CSSO: 1%Eu²⁺ and CSSO: 1%Eu²⁺, 3%S²⁻ samples are measured as shown in Fig. 5a, S12 and S13. The thermal stability of CSSO: 1%Eu²⁺, 3%S²⁻ (51%@120°C) is significantly improved compared with that of CSSO: 1%Eu²⁺ (33%@120°C) sample. Generally, the thermal quenching behavior can be expressed by the configuration coordinate diagram in Fig. 5b. As the temperature increases, the electrons at the lowest 5d level gain more energy, overcoming the energy barrier and resulting in thermal quenching behavior (i.e. A→B→C→F→D→A). Among these transitions, the energy difference from C to F indicates the difficulty of this thermally activated process, this is, the activation energy (ΔE), which can be determined by the Arrhenius formula,[51]

$$I(T) \approx \frac{I_0}{1+c\exp(-\frac{\Delta E}{kT})} \quad (3)$$

Where I(T) is the emission intensity at temperature T(K), I₀ is the initial emission intensity, c is a constant related to the host material and k is Boltzmann's constant. By rearranging equation (3) and plotting ln[(I₀/I_T)-1] against 1/kT, as shown in Fig. 5c, the thermal activation energy ΔE₂ is calculated to be 0.2933 eV, which is higher than the ΔE₁ (0.2865 eV). This is consistent with the better thermal stability of CSSO: 1%Eu²⁺, 3%S²⁻ sample. The bond energy of [Sc/Eu-O/S] is higher than that of the [Sc/Eu-O] when the S²⁻ enters the CSSO: 1%Eu²⁺ sample, the valence electrons of Eu²⁺ in the outer layer strongly interact with the lattice environment, resulting in the rigid lattice structure and achieving a large activation energy ΔE.[52] Huang's theory indicates that the value of ΔE has dependence on the strength of electron-phonon coupling, reflected by the Huang-Rhys factor and obtained via the following formula,[53]

$$\text{FWHM}(T) = \sqrt{8\ln 2S}(h\nu) \sqrt{\coth\left(\frac{h\nu}{2kT}\right)} \quad (4)$$

Where S is the Huang-Rhys factor, $h\nu$ is the mean phonon energy, and k is the Boltzmann's constant. S is determined to be 4.94 and 4.87 for CSSO: 1% Eu^{2+} and CSSO: 1% Eu^{2+} , 3% S^{2-} samples (Fig. 5d), respectively. The smaller S for CSSO: 1% Eu^{2+} , 3% S^{2-} sample indicates that the electron-phonon coupling is weaker than CSSO: 1% Eu^{2+} sample, and the spectral broadening is less as the temperature increases (Table S9), which also contributes the excellent thermal quenching properties.[54]

Moreover, we measured the decay curves of the CSSO: 1% Eu^{2+} , 3% S^{2-} sample in the temperature range of 30 to 240°C as shown in Fig. S14 and Table S10. The lifetime decreases from 5.05 to 4.52 μs as the temperature increases. This indicates that the interaction between Eu^{2+} ions diminish at high temperature.[55, 56] In order to further prove that CSSO: 1% Eu^{2+} , 3% S^{2-} sample possesses excellent thermal stability and more spectral details, the emission spectrum of CSSO: 1% Eu^{2+} , 3% S^{2-} sample is measured at 77K, as shown in Fig. 5e. The emission intensity of the sample at 77K remains 8.33 times that at 300K, indicating that the optimal sample still exhibits high emission efficiency at low temperatures. In addition, we also studied the luminescence stability of CSSO: 1% Eu^{2+} , 3% S^{2-} in humid environments at 85°C and 85% humidity for ten days as shown in Fig. 5f. The results indicate that the sample can still maintain good stability in humid environments.

2.6 The application of CSSO: 1%Eu²⁺, 3%S²⁻ sample for pc-NIR LED.

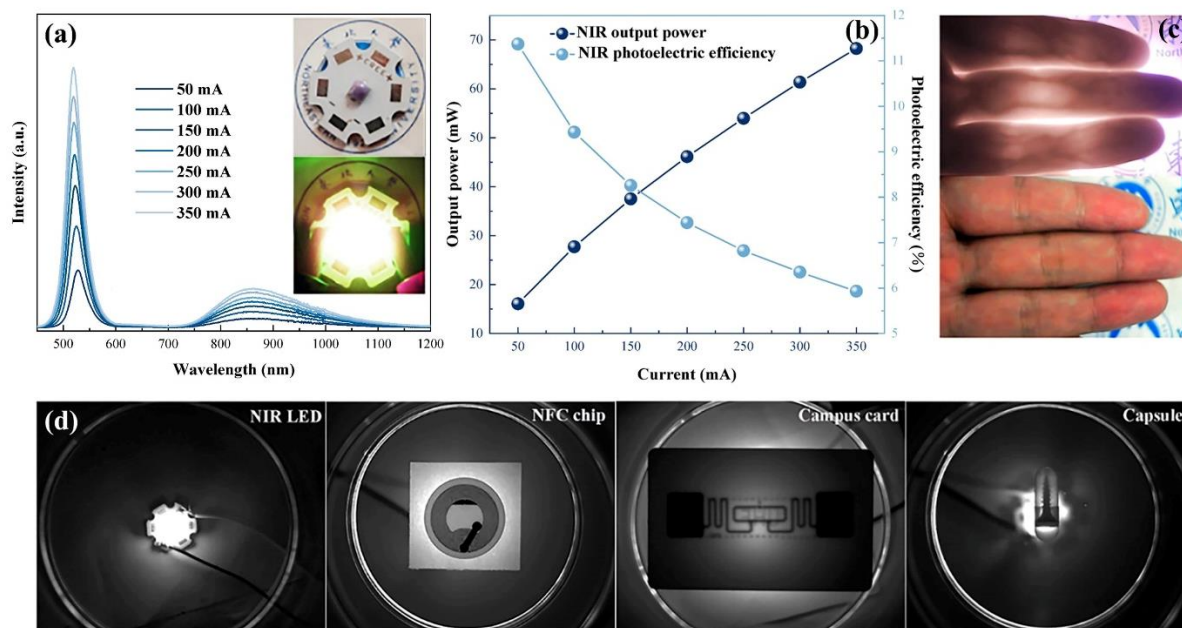


Figure 6(a) Electroluminescent spectra of the fabricated pc-NIR LED under different drive current, inset shows the fabricated pc-NIR LED with the light off and on; (b) The NIR output power and photoelectric efficiency under different drive current; (c) Vein imaging; (d) Photographs of the pc-NIR LED, NFC chip, campus card and capsules taken by the NIR camera.

Finally, a pc-NIR LED is fabricated by coating the CSSO: 1%Eu²⁺, 3%S²⁻ sample on a commercial 520 nm LED chip, and the photoelectric efficiency of the pc-NIR LED is measured as shown in Fig. 6a and b. It can be clearly observed that the NIR luminous intensity is enhanced with increase of driving current, resulting in the output power increases from 16.09 mW@50 mA to 68.22 mW@350 mA, while the conversion efficiency decreases from 11.37%@50 mA to 5.93%@350 mA. Furthermore, the electroluminescent performance of the pc-NIR LED is compared with that of similar green light-excited pc-NIR LEDs, the commercial pc-NIR LEDs (Osram SHF 4735 and 4776) and other blue light-excited pc-NIR LEDs, as shown in Table S11. The results shows that our prepared pc-NIR LED has excellent NIR output power and conversion efficiency at drive current of 100 mA, which are significantly superior to those of other green or blue light excited pc-NIR LEDs, and even more superior compared with the

commercial Osram pc-NIR LEDs at driven current of 350 mA. The operating temperature of the pc-NIR LED for currents ranging from 100 to 350 mA is shown in Fig. S15, and the temperature increases from 26.1 to 51.4°C. Additionally, we recorded a temperature increase from 31.9 to 57.2°C when driving the pc-NIR LEDs for 30 to 90 min at 100 mA. Moreover, Figure 6c shows the application for human vein imaging, indicating great potential in the field of biomedical imaging. Meanwhile, benefiting from the high penetrating power of NIR light from the designed pc-NIR LED, the inner structure and some hidden details of the opaque objects (such as NFC chip, campus card and capsules) can be clearly detected, as shown in Fig. 6d and S16. Overall, the fabricated pc-NIR LED shows great potential applications in non-destructive inspection and biomedical imaging.

3. Conclusion

In this work, we have successfully synthesized a series of Eu^{2+} doped NIR-emitting sulfured garnet phosphors $\text{CSSO: Eu}^{2+}, \text{S}^{2-}$. The broad NIR emission centered at 860 nm corresponds to the $5d \rightarrow 4f$ transition of Eu^{2+} occupying 6-coordinated Sc^{3+} sites rather than 8-coordinated Ca^{2+} sites through chemical unit co-substitution strategy. Importantly, we proposed two methods to optimize the NIR emission of garnet phosphor CSSO: Eu^{2+} . Firstly, the prepared EuS is used instead of the traditional Eu_2O_3 as the raw material to regulate the initial valence state of the dopant, enhancing the NIR emission by 135%. Secondly, the sulfuration strategy can further enhance the NIR-emitting intensity and internal quantum efficiency by 192% and 167.8%, and the thermal stability is improved by 154% @ 120°C. It can be seen that both the utilization of pre-prepared EuS and the sulfuration strategy are equally crucial in enhancing the

luminous intensity of CSSO: Eu²⁺ phosphors. Finally, a pc-NIR LED is fabricated with excellent photoelectric efficiency of 9.43%@100 mA and NIR output powers of 22.74 mW@100 mA. Its performance is superior to that of some other green or blue light-excited pc-NIR LEDs, and offers potential applications in nondestructive internal defect detection and vein imaging. In summary, this work not only confirms the luminescence origin of Eu²⁺-doped garnet NIR-emitting phosphor, but also provides two new strategies to achieve high-performance NIR luminescence of Eu²⁺, encouraging further researchers into efficient Eu²⁺-doped garnet NIR-emitting phosphor for photonic applications.

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