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Enhancing blue light absorption by Sm$^{3+}$ Co-doing in Ca9Nd(PO$_4$)$_7$: Eu$^{3+}$ for white light-emitting diodes

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Abstract

White light-emitting diodes (WLEDs) is widely concerned as the next-generation source of displays and lighting on account of many advantages. In this work, Sm$^{3+}$ ions were introduced into Ca$_9$Nd(PO$_4$)$_7$: Eu$^{3+}$ (CNPO: Eu$^{3+}$) red phosphors as a co-dopant to boost the blue-light excitation. X-ray diffraction (XRD) data confirm the successful preparation of the materials. Rietveld refinements were employed to investigate the site occupation and lattice parameter variation. All obtained materials have showed red emission under blue light or near-ultraviolet light excitation. The photoluminescence (PL) emission spectra features both signals from the two dopants, and the introduction of Sm$^{3+}$ could effectively boost the red-light emission and blue-light excitation. Theoretical simulations help evidence the capability of the CNPO materials as host matrix of luminescent centers. Finally, a blue LED chip-based WLED was assembled in demonstration of their potential applications. Compared to the controlling device made with Eu$^{3+}$ single-doped samples, the co-doped one has stronger blue light excitation and red light emission that guarantees a high luminous efficacy of over 90 lm W$^{-1}$. The device also shows a superb long-term stability under continuous working. All in all, the CNPO: Eu$^{3+}$, Sm$^{3+}$ phosphors have shown many promising aspects in blue chip-based WLED applications.

1. Introduction

Solid-state light sources have been widely regarded as the next-generation media of lighting and displays [1]. The combination of long product lives, high conversion efficiency, and facile industrial preparation ensure their prospects in practical applications. Nowadays, most of the conventional white light-emitting diodes (WLEDs) consist of a blue-light emitting chip and yellow YAG: Ce$^{3+}$- phosphors [2]. The facile preparation and high quantum efficiency of YAG: Ce$^{3+}$ phosphors have granted them a dominant place. However, they do show disadvantages of low color rendering index and high color temperature due to the lack of color rendering index component [3]. Another fabrication method that introduces an additional red light source has shown many merits, such as the enhanced color rendering property and lowered color temperature that is friendly to human eyes [4, 5].

Eu$^{3+}$ ions are regarded as ideal red light-emitting activators for the high quantum efficiency and high color purity [6–8]. Compared to other activators, such as Mn$^{2+}$ or Mn$^{4+}$, the stability of Eu$^{3+}$-based materials is also relatively high [9–14]. Additionally, aiming to broaden the excitation range of such activators, sensitizers are commonly introduced into the lattice to realize energy transfer. According to the present literature, many candidates have chosen to expand the excitation band of Eu$^{3+}$ luminescent center by the co-doping or multi-doping strategies, such as Ce$^{3+}$ [15], Tb$^{3+}$ [16], and Bi$^{3+}$ [17, 18]. Among all potential co-doping candidates,
Sm$^{3+}$ is regarded as one of the most effective ones by many groups [19]. The energy can be easily transferred from $^4G_{5/2}$ of Sm$^{3+}$ to $^7D_1$ of Eu$^{3+}$ via photon-assisted energy transfer [19]. The emission peaks of Sm$^{3+}$ itself are also often located in the red region that is close to the emission peaks of Eu$^{3+}$ (usually from 608–613 nm dependent on the environments) [20]. Therefore, It is important to find a proper host matrix with high thermal stability to hold this pair of sensitizers and activators.

Phosphate materials possess the merits of relatively low preparing temperatures, high quantum efficiencies, and good stabilities [21–24]. Many pieces of literature have focused on phosphate-type materials as phosphors in WLED applications, such as NaSrPO$_4$:Eu$^{3+}$ [22], AlPO$_4$:Eu$^{3+}$ [23], Ca$_{10}$Li$_2$(PO$_4$)$_2$ [26], and Ca$_3$Sr$_2$(PO$_4$)$_4$ [27]. Among all phosphate candidates, the $\beta$-Ca$_3$(PO$_4$)$_2$ and its multi-cation derivates with sufficient room for structural regulations were a research hot spot for many years [28, 29]. In this work, a new type of Ca$_9$Nd(PO$_4$)$_2$ (abbreviates as CNPO according to the formula) host material was designed and synthesized by cationic substitution, (i.e. replacing metal cations with other homovalent or heterovalent metal) based on Ca$_3$(PO$_4$)$_2$ [21, 29]. And the CNPO was then chosen as the host materials to prepare a series of Eu$^{3+}$-doped phosphors. To further boost the blue light absorption, a co-doping strategy is applied in this type of material. In this paper, CNPO: Eu$^{3+}$ red phosphors were first prepared before various amounts of Sm$^{3+}$ ions were introduced into the lattice as co-dopants. The X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses help in confirming the homogeneity before and after the introductions of dopants. Optical properties were then studied by both spectra characterization and theoretical simulations. The quenching mechanism and the energy transfer mechanism were investigated in detail to reveal the high thermal stability of the materials. Finally, a blue chip-based WLED prototype device was made in comparison with the one without Sm$^{3+}$ sensitizer to demonstrate an enhanced luminous efficacy after broadening the blue light excitation of the materials by Sm$^{3+}$ co-doping. Such research provides insight into realizing high-performance phosphors by co-doping.

2. Materials and methods

2.1. Preparations of CNPO: Sm$^{3+}$, CNPO: Eu$^{3+}$, and CNPO: Eu$^{3+}$, Sm$^{3+}$

A series of CNPO: Eu$^{3+}$ samples with different doping concentrations were synthesized via solid-state reaction. Nd$_2$O$_3$, (NH$_4$)$_2$HPO$_4$, CaCO$_3$, were weighted together with designed amount of Eu$_2$O$_3$ and/or Sm$_2$O$_3$ before the mixture is grounded thoroughly. The materials were then heated at 1423 K for 10 h and followed by 1598 K calcination for another 5 h. The final powders were collected and washed with absolute ethanol twice before being dried in a vacuum oven at 353 K overnight.

2.2. Characterizations

A D8 Focus diffractometer was employed to acquire XRD data. Rietveld refinement was carried out via Fullprof software. SEM images were captured with a MIRA5-LMH microscope. The photoluminescence emission (PL) and excitation (PLE) spectra were recorded on a Hitachi F-8000, which is also utilized to collected temperature-dependent PL spectra and PL decay curves. A 460 nm blue LED chip (GUHON company) was used as the basement of the WLED together with commercial YAG:Ce$^{3+}$ yellow phosphors (Intematix). Another device was made by the same component with additional CNPO: Eu$^{3+}$ or CNPO: Eu$^{3+}$, Sm$^{3+}$ as the red component, respectively.

2.3. Simulation methods

The full structure optimizations and the electronic property calculations employed the Vienna $ab$ $initio$ simulation package (VASP) within the DFT framework. The plane-wave basis set and projector augmented wave (PAW) potentials were used to define the electronic wave functions. The Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional. The structure was first allowed to relax with the electronic convergence criteria set to $5 \times 10^{-4}$ eV and the ionic relaxation was set to 0.05 eV/Å. Cutoff energy of 400 eV was employed with a Monkhorst-Pack k-point grid of $2 \times 2 \times 2$.

3. Results

3.1. Crystal structures and morphologies

The phases of the materials were first checked with XRD measurements. (figure 1(a)). With reference to the standard data of JCPDS card PDF# 45-0346CNPO (PDF# 45-0346 of JCPDS cards), all the obtained materials have shown no signs of obvious impurities or orientation, which suggests that the designed materials have been successfully synthesized. Besides, there are slight shifts in peak locations that correspond to the dopant effect of Sm/Ca or Eu/Ca substitution. For instance, as can be seen from the enlarged XRD patterns around 31° in figure 1(b), a regular shift towards the high-angle direction can be observed upon increased Sm$^{3+}$
concentration, and the corresponding angle of Eu$^{3+}$ single-doped sample is also slightly larger than the PDF reference. Such shift also proves the successful introduction of Eu$^{3+}$ and/or Sm$^{3+}$ dopants, as well as pointing out the fact that these material systems could form a regular CNPO: Eu$^{3+}$, Sm$^{3+}$ solid solutions within relatively small doping amounts. To further shed light on the morphologies and element distributions of the obtained samples, SEM photos were captured and the elemental mapping based on energy dispersive spectrometer (EDS) was acquired (figures 2 and S1; S2 available online at stacks.iop.org/MRX/8/096201/mmedia). It is found that the particles of Eu$^{3+}$-doped sample were irregular polyhedrons with $\sim$5 $\mu$m in dimensions (figure S1(b)), and all elements including Eu were evenly dispersed without obvious aggregation. The morphologies were retained after introducing Sm$^{3+}$ (figure 2(a)), and the elements are as well uniformly distributed, indicating the successful preparation of these co-doped materials (figures 2(c)–(h)). Figure 2(b) shows the EDS diagram of the materials. The integrated results reflecting the element ratio match well with the designed formula, which evidence the good quality of the as-prepared samples.

It has been widely reported that the double calcium metal phosphate structures (with formula Ca$_9$R(PO$_4$)$_7$ where R is a metal) crystallize in the R3c space group. The structures can be regarded as derivatives of whitlockite or $\beta$-Ca$_3$(PO$_4$)$_2$ by certain types of cationic substitution [30]. Since many polyvalent metal cations are included in the potential list of candidates, the number of derivatives is numerous which guarantees enough places for structural modifications towards optimum properties [31]. So the cationic substitution strategy is able to perform as a basic methodology in the structural design of functional materials in many aspects including phosphors and nonlinear optical materials [32].

The $\beta$-Ca$_3$(PO$_4$)$_2$-type crystal structures have been a research hotspot for years [33, 34]. It is known that the five cationic sites in the structures each has different chemical environments [35]. Ca originally occupies all these sites in spite of Ca4 which has an occupation of 50% Ca and 50% vacancy. Tailored structures have been designed by different substitutions of metal ions and/or vacancies in these cationic sites [36]. In our work, the proposed matrix material CNPO was generated by substituting two trivalent metal ions into Ca sites [37, 38]. Compared to the mother structure of $\beta$-Ca$_3$(PO$_4$)$_2$, CNPO possesses as many as four cationic sites (M1, M2, M3, and M5), while the original M4 site was left as some other vacancies to keep the overall charge in the lattice balanced. It is reported that the site occupation in CNPO is dependent on the dopant ions to be taken into the matrix [39]. When introducing dopants between La and Eu in the element table, the M1, M2 or M4 tend to be replaced by these kinds of dopants. On the other hand, when R is chosen from Tb to Lu, the dopant ions would
take the place of M1, M2, and M5 sites. In addition, the M5 site is stable considering its tight octahedral coordination since it can only be replaced when small cations are introduced like Fe\(^{3+}\) and In\(^{3+}\).

In the host CNPO, the M1, M2, M3 and M5 sites orderly possess the 8, 7, 8, and 6 as their coordination number (CN). The M4 and M5 have a higher site symmetry than the rest cationic sites (Wyckoff site is 6a versus 18b). In that case, Nd\(^{3+}\) (the ionic radius is \(\sim 0.995\) Å) would be more likely to take into the M1, M2 and M3 sites. Rietveld refinements were then carried out to figure out the actual site occupation and the corresponding lattice parameters of the single- and co-doped samples. \(\beta\)-Ca\(_3\)(PO\(_4\))\(_2\) \((R3c)\) was employed as the starting model since the crystal data of the CNPO host structure are unavailable in the present database system. The refinement result is listed in figure 3 together with trustworthy R factors that are all below 10\% (the Rp value is 6.21\%, and Rwp is 9.45\%). Some key parameters of the refinement results are listed in table S1. All the information on bond lengths and average lengths can be found in table S2. The refinement result of Eu\(^{3+}\) single-doped sample and the 0.8\% Sm\(^{3+}\)-doping sample was presented in figures S3 and S4, respectively, where some minor impurities were found especially for the former one, indicating that further Sm\(^{3+}\) doping might be difficult to achieve. Therefore, the doping concentration was settled within small values to ensure the purity of the samples.

The refined crystal structures of the obtained samples are shown in figure 4. In the diagram, all the distorted [CaO\(_x\)] polyhedrons, in which some of the cationic Ca sites were partly substituted by other metal cations, could form a condensed face-sharing framework that is able to ensure a considerably high condensation degree and rigidity of this structure. Therefore, the rigidity of the structure is high and beneficial to its stability in many aspects. Since the Ca\(^{2+}\) ionic radii with different CNs are all around \(\sim 2.0\) Å, the numbers of alternative cations in the lattice could represent the crystal lattice energy as described in the Born-Lande formula [40], which will decrease with a larger distance between the coordination center and the ligands in a polyhedron. As listed in table 1, generally, the Ca4–O bond length can be found as the smallest one. In that case, the dopant Sm\(^{3+}\) and Eu\(^{3+}\) tend to substitute the other Ca sites in spite of the octahedral coordination of Ca4. The Baur’s distortion indices \(\Delta\) can present evidence from another perspective as given by (equation (1)):
where $R_i$ is the value of the bond length of the $i$'s bond, and $\bar{R}$ represents the mean bond length in the structure. The data acquired based on the refined crystal data are listed in table 1. The Ca4 octahedron possesses the smallest distortion index both before and after being introduced with dopants, and the value only changes slightly. The results could suggest the fact that [Ca4O6] is likely to be absent in the doping process. On the other
hand, the indices of Ca1, Ca2 and Ca3 polyhedron all change to a relatively large extent, and their average bond lengths are also comparatively large that makes these sites favorable for dopant incorporation of Sm$^{3+}$ and Eu$^{3+}$.

3.2. Theoretical simulations
The Vienna ab initio simulation package (VASP) was then employed to shed light on the crystalline and electronic structures theoretically based on the density functional theory (DFT) [41, 42]. After geometry optimization applying the same criterion, the total energies of the systems were minimized to give lattice parameters of $a = 10.40382$ Å, $b = 10.40382$ Å and $c = 37.32860$ Å, which does not deviates very much from the refinement results. Figures 5(a) and (b) show the electronic band structure as well as the total density of states (DOS) and partial DOS of the host CNPO materials, respectively. The CNPO host is an indirect wideband semiconductor, and the valence band maximum (VBM) is found at the $F$ point in the $k$-space, while the conduction band minimum (CBM) is located at the Gamma point. The width of the forbidden gap between the VBM and CBM is approximately 4 eV, the value of which is large enough for the doping of other luminescent centers, like Sm$^{3+}$ or Eu$^{3+}$ in this work. The DOS and partial DOS could give the composition of the CB and VB. It was found that the VBM is mostly contributed by P (2p) states and O (2p) states, while the CBM is mainly originated from Nd (5d) states. The theoretical simulation results suggest that the CNPO hosts are promising candidates as the host matrix for doping luminescent centers such as in our case, Sm$^{3+}$ and Eu$^{3+}$.

![Figure 5](image.png)

Figure 5. The energy band structure (a) and DOS (b) of CNPO.

| Sample          | Polyhedron          | Average bond lengths (Å) | Distortion index |
|-----------------|---------------------|--------------------------|------------------|
| CNPO            | [Ca1O$_8$]         | 2.4715                   | 0.06270          |
|                 | [Ca2O$_7$]         | 2.4745                   | 0.06724          |
|                 | [Ca3O$_8$]         | 2.5836                   | 0.03812          |
|                 | [Ca4O$_6$]         | 2.2320                   | 0.01259          |
| CNPO: Eu$^{3+}$ | [Ca1O$_8$]         | 2.4391                   | 0.03018          |
| Sm$^{3+}$       | [Ca2O$_7$]         | 2.4858                   | 0.04550          |
|                 | [Ca3O$_8$]         | 2.5599                   | 0.03870          |
|                 | [Ca4O$_6$]         | 2.2843                   | 0.00126          |
| CNPO: Eu$^{3+}$ | [Ca1O$_8$]         | 2.4331                   | 0.02908          |
|                 | [Ca2O$_7$]         | 2.4332                   | 0.03022          |
|                 | [Ca3O$_8$]         | 2.5565                   | 0.04052          |
|                 | [Ca4O$_6$]         | 2.2828                   | 0.00259          |
| CNPO: Sm$^{3+}$ | [Ca1O$_8$]         | 2.4392                   | 0.03035          |
|                 | [Ca2O$_7$]         | 2.4859                   | 0.04561          |
|                 | [Ca3O$_8$]         | 2.5601                   | 0.03890          |
|                 | [Ca4O$_6$]         | 2.2841                   | 0.00078          |
3.3. Luminescent properties

A series of Eu\(^{3+}\) single-doped materials were first synthesized to find the optimal Eu\(^{3+}\) concentration. As the luminescence emission (PL) spectra shown in figure S5, the maximum PL intensity was found at \(-0.5\%\). So, the co-doping experiments employ 0.5% as the Eu concentration. The PL and excitation (PLE) spectra of the co-doped samples CNPO: Eu\(^{3+},\) Sm\(^{3+}\) are shown in figure 6, with the single Eu\(^{3+}\)-doped CNPO as the comparison. As for the PLE one in figure 6(a), the intense peak at \(-392\) nm is ascribed to the transition of \(4F_7/2\) of Eu\(^{3+}\), while the new peak appeared at \(-403\) nm compared to the Eu\(^{3+}\) single-doped one is originated from the \(6H_{15/2}^{-}F_{7/2}\) transition of the Sm\(^{3+}\) ions. Also, the \(4F_{9/2}^{-}D_{2}\) transition has been greatly strengthened by Sm\(^{3+}\) co-doping compared to the control experiments of Eu\(^{3+}\) ion single-doped samples. In the PL spectra shown in figure 6(b), both signals from the Eu\(^{3+}\) and Sm\(^{3+}\) luminescent centers can be detected, and the transitions have been tagged next to the corresponding PL peaks. The PL peaks located at 572, 598, 609, 613, 619, 653, and 701 nm can be assigned to the \(6G_{5/2}^{-}F_{5/2}\) (from Sm\(^{3+}\)), \(5D_0^{-}F_0\) (from Eu\(^{3+}\)), \(5D_0^{-}F_1\) (Eu\(^{3+}\)), \(4G_{5/2}^{-}F_{7/2}\) (Sm\(^{3+}\)), \(5D_0^{-}F_2\) (Eu\(^{3+}\)), \(4G_{5/2}^{-}F_{9/2}\) (Sm\(^{3+}\)), and \(5D_0^{-}F_4\) (Eu\(^{3+}\)), respectively. It can be seen from the results that the Sm\(^{3+}\) co-doping has contributed to an enhanced red-light emission at \(-610\) nm in spite of the near-infrared ones (\(-700\) nm) with reference to the Eu\(^{3+}\) ion single doped controlling samples. The excitation intensity in the blue light region has also been enhanced for the co-doped samples compared to the Eu\(^{3+}\) ion single-doped references. Therefore, the overall co-doping effect that increases the red-light emission with blue light excitation will benefit the application of these materials in displays and lightings. Additionally, compared to the concentration-dependent Eu\(^{3+}\) single-doped PL spectra in figure S5, the Sm\(^{3+}\) co-doping strategy seems more convincing to practical regulation of the luminescent properties of these materials.

From both the above PL and PLE spectra, one may find that the intensities of the samples with the same Eu\(^{3+}\)-doping concentration enjoy a linear enhancement with increasing Sm\(^{3+}\) dosage. Such results indicate that the host materials may prevent the interaction between the luminescent centers to some extent. We then estimated the critical distance (R\(_c\)) of intra-luminescent center interaction of this host matrix by following equation (2) [43]:

\[
R_c \approx 2(3V/4\pi \chi_c N)^{1/3}
\]  

In the equation, \(N\) is the number of cationic site atoms and \(V\) the cell volume of the lattices. \(\chi_c\) could present an optimum concentration found in the experiments. In that case, one may put the following parameters in the equation: \(\chi_c = 1.0, V = 3560.1395\ \text{Å}^3, N = 6\). Then, R\(_c\) can be calculated as 17.34 Å, which is an extremely large distance that assures more incorporation of luminescent centers or sensitizer with reference to the range of exchange interaction (whose R\(_c\) is \(-5\) Å).

The PL decay curves of the as-prepared samples of CNPO: Eu\(^{3+},\) Sm\(^{3+}\) were recorded monitoring the 609 nm emission by 365 nm excitation as exhibited in figure 7. The decay curves can be fitted bi-exponentially as:

\[
y = y_0 + A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}
\]

where \(\tau_1\) is the lifetime of exciton recombination pathway of the emission and \(\tau_2\) the lifetime of defect-related PL process, while their weights are represented by \(A_1\) and \(A_2\), respectively. The acquired data were plotted. The \(\tau_1\) values are 63.6, 82.5, 120.3, 113.1, and 143.1 \(\mu\)s, respectively as listed in table 2, which is close to that of...
Eu\textsuperscript{3+}-single doped samples at the beginning but keeps increasing with more Sm\textsuperscript{3+} doping. Compared to Eu\textsuperscript{3+} single doped ones, which can be fitted by a single exponential function (figure 7(a)), the extra recombination pathway represented by $t_2$ that prolongs the whole decay process may be derived from the energy transfer process \[44\]. This pattern illustrates the only crystallography environment of Eu\textsuperscript{3+} in the CNPO. Since the PL decay lifetime can be determined by the time assumption for the intensity ($I_t$) to decrease to $1/e$ of the pristine value ($I_0$), until the fluorescent quenching effect takes place, the radiative recombination in the systems contributes mainly to the PL decay lifetimes rather than non-radiative ones. In addition, the average PL decay lifetime is determined by the following equation (4):

$$\tau_{\text{average}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

In that case, the average decay lifetime of Sm\textsuperscript{3+} co-doped samples are estimated as 171.34, 242.88, 303.38, 350.36, and 410.72 $\mu$s, respectively, which is much larger than the pristine single-doped one. The relatively short decay lifetimes of the as-prepared materials could benefit their applications in display- and lighting-related fields.

### 3.4. WLED application

The enhanced blue light excitation makes the above materials favorable for blue LED-based white light-emitting applications. We thus assembled a WLED device to evidence the practical application prospects of CNPO: Eu\textsuperscript{3+}, Sm\textsuperscript{3+}. The above phosphors and commercial YAG: Ce\textsuperscript{3+} yellow phosphor were mixed with silica adhesive thoroughly and coated uniformly on a 460 nm blue LED chip before solidification by ultraviolet flashlight. The obtained WLED was tested under 20 mA driven current. The output spectrum was recorded and presented in figure 8 with bright and warm white light. The CIE coordinates are (0.36, 0.38) with a high Ra value of 78.7. The presence of red components from CNPO: Eu\textsuperscript{3+}, Sm\textsuperscript{3+} can increase the color rendering index while decreasing the color temperature compared to the conventional YAG: Ce-based WLED devices as reported in other literature. Such warm and efficient white light is not only favorable to many lighting scenarios but also healthier to the human eyes. A controlling WLED with Commercial composition (Blue chip + YAG yellow phosphor) has also been assembled for a clear comparison. The output spectrum was shown in figure S6. The device presented a cold white light with a high Tc of 7520 K and the CIE coordinates of (0.30, 0.31), while the luminous

### Table 2. Fitted lifetimes and average lifetimes, in $\mu$s.

| Sample                  | $\tau_1$ | $A_1$ | $\tau_1$ | $A_2$ | $\tau_{\text{average}}$ |
|-------------------------|----------|-------|----------|-------|-------------------------|
| CNPO:0.5Eu\textsuperscript{3+} | 58.4     | null  | null     | null  | 171.34                 |
| CNPO:0.5Eu\textsuperscript{3+}, 0.2Sm\textsuperscript{3+} | 63.6     | 2909.96 | 216.26   | 2052.99 | 242.88                 |
| CNPO:0.5Eu\textsuperscript{3+}, 0.4Sm\textsuperscript{3+} | 82.5     | 3081.33 | 311.31   | 1913.95 | 303.38                 |
| CNPO:0.5Eu\textsuperscript{3+}, 0.6Sm\textsuperscript{3+} | 120.3    | 3541.94 | 420.24   | 1588.70 | 350.36                 |
| CNPO:0.5Eu\textsuperscript{3+}, 0.8Sm\textsuperscript{3+} | 113.1    | 2764.20 | 434.43   | 2031.12 | 303.38                 |
| CNPO:0.5Eu\textsuperscript{3+}, 1.0Sm\textsuperscript{3+} | 143.1    | 3305.43 | 544.80   | 1732.96 | 410.72                 |

![Figure 7. PL decay curves for various Sm\textsuperscript{3+} co-doped CNPO: 0.5Eu\textsuperscript{3+}, and compared to those of (b) various Eu\textsuperscript{3+} single doped CNPO.](image)
efﬁcacy is 138.6 lm W\(^{-1}\) at 20 mA working conditions. It is worth mentioning the CNPO:Eu\(^{3+}\), Sm\(^{3+}\)-included WLED also has a high luminous efﬁcacy of ≈100 lm W\(^{-1}\) at the same conditions. More parameters of the CNPO: Eu\(^{3+}\), Sm\(^{3+}\) WLED from R1 to R15 can be found in table S3. In contrast, the Eu\(^{3+}\) single doped one has a relatively lower luminous efﬁcacy of ≈45 lm W\(^{-1}\) due to the weak blue light excitation (ﬁgure S7). Furthermore, we tested the long-term stability of the as-fabricated device. The WLED was driven by 20 mA and forced to work continuously for a long period of more than 20 h. Since the working temperature of a LED is usually high above 60 °C if not even higher [14, 45, 46], both thermal stability of luminescent properties and the structure rigidity are required in this process. Luckily, the as-assemble device survived such a severe condition without any drops in luminous efﬁcacy. The efﬁcacies only ﬂuctuated over the whole period around 99 lm W\(^{-1}\) (ﬁgure 7(b)), which will deﬁnitely beneﬁt the practical application of this device. The above data all indicate the fact that CNPO:Eu\(^{3+}\), Sm\(^{3+}\) has a promising potential in blue chip-based WLEDs application.

4. Conclusion

In summary, Sm\(^{3+}\) ions were introduced into CNPO: Eu\(^{3+}\) to increase their luminescent properties. The phosphors can be prepared by facile high-temperature solid-state reaction. The phase and morphologies indicate the high quality of crystallinity. Further XRD reﬁnements were performed using the XRD data to back up the successful preparation. DFT simulation was employed to prove the CNPO as an intriguing promising host matrix for luminescent centers. The CNPO: Eu\(^{3+}\), Sm\(^{3+}\) phosphors showed better luminescent performance compared to the Eu\(^{3+}\) single doped one, and the critical interaction distance is as high as 17.34 Å. Introducing Sm\(^{3+}\) was also proved to have a better effect than increasing the Eu\(^{3+}\) concentration. The PL decay lifetimes of the as-prepared CNPO: Eu\(^{3+}\), Sm\(^{3+}\) samples are found to be bi-exponential due to the inner energy transfer process. In the end, a WLED was fabricated by employing CNPO: Eu\(^{3+}\), Sm\(^{3+}\) and the controlling CNPO:Eu\(^{3+}\) sample as the red phosphor, respectively. The former device presents a high luminous efﬁcacy of near 100 lm W\(^{-1}\) that could last for a long period with continuous working conditions. On the other hand, the one made with the single-doped sample has possessed a relatively low efﬁcacy due to the weak blue light excitation. The research has demonstrated a great potential of the as-prepared CNPO: Eu\(^{3+}\), Sm\(^{3+}\) as a novel and promising red phosphor in the ﬁeld of blue LED chip-based WLEDs application.

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Data availability statement

All data that support the ﬁndings of this study are included within the article (and any supplementary files).
Declarations of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References
[1] Ye S, Xiao F, Pan Y X, Ma Y Y and Zhang Q Y 2010 Phosphors in phosphor-conversion white light-emitting diodes: Recent advances in materials, techniques and properties Materials Science and Engineering: R: Reports 71 1–34
[2] Park J K, Kim C H, Park S H, Park H D and Choi S Y 2004 Application of strontium silicate yellow phosphor for white light-emitting diodes Appl. Phys. Lett. 84 1647–9
[3] Yamada M, Naitou T, Izuou K, Tamaki H, Murazaki Y, Kameshima M and Mukai T 2003 Red-enhanced white-light-emitting diode using a new red phosphor Jpn. J. Appl. Phys. 42 L20–3
[4] Zhou Q, Zhou Y, Liu Y, Luo L, Wang Z, Peng J, Yan J and Wu M 2015 A new red phosphor BaGeF2:Mn4+: hydrothermal synthesis, photo-luminescence properties, and its application in warm white LED devices J. Mater. Chem. C 13 3055–9
[5] Zhong J, Chen D, Zhao W, Zhou Y, Hu H, Chen L and Ji Z 2015 Garnet-based Lu3La5S12:Eu3+ red phosphors: a potential color-converting material for warm white light-emitting diodes J. Mater. Chem. C 17 4500–10
[6] Huang X, Li B, Guo H and Chen D 2017 Molybdenum-doping-induced photoluminescence enhancement in Eu3+-activated CaWO4 red-emitting phosphors for white light-emitting diodes J. Phys. Chem. C 121 1495–502
[7] Y-F L, Z-P Y and Q-M Y 2011 Preparation and its luminescent properties of AlPO4:Eu3+ phosphor for w-LED applications J. Alloys Compd. 509 L199–202
[8] Yang R, Cheng F, Zhao Y and Ye S 2020 Probing the Dielectric effects on the colloidal 2D perovskite oxides by Eu3+ luminescence ACS Appl. Mater. Interfaces 12 44961–9
[9] Huang L, Zhu Y, Zhang X, Zou R, Pan F, Wang J and Wu M 2016 HF-free hydrothermal route for synthesis of highly efficient narrow-band red emitting phosphor K2Si1−xFexMn4+: solid state reaction ECS J. Solid State Sci. Technol. 3 R57–61
[10] Hou I S, Jiang W Z, Fang Y Z, Wang Y M, Yin X and Huang F Q 2012 Red-Emitting Ca2Al(P2O10):Ce4+,Mn2+ phosphor with energy transfer prepared by solid state reaction ECS J. Solid State Sci. Technol. 3 R57–61
[11] Ming-Zhao L, Zhan-Lan Y, Li Z, Shi-Fu W and Jin-Guang W 2002 Photoluminescence of Acta Phys. - Chim. Sin. 18 668–72
[12] Zhou Q, Dolgov L, Srivastava A M, Zhou L, Wang Z, Shi J, Djamamicin M D, Brik M G and Wu M 2018 Mn3+ and Mn4+ red phosphors: synthesis, luminescence and applications in WLEDs, a review J. Mater. Chem. C 6 2652–71
[13] Zhou W, Wang R H, Yin L, Chen S, Xu C, Xing X and Liu R S 2019 Alcohol-guided growth of two-dimensional narrow-band red-emitting K2Te5Mn4+ for white-light-emitting diodes ACS Appl. Mater. Interfaces 11 20143–9
[14] Ming H, Zhao Y, Zhou Y, Zhang S, Wang Y, Song E, Xia Z and Zhang Q 2020 A Guanidinium-Based Mn3+/Mn4+ - Doped Red-Emitting Hybrid Phosphor with High Stability ACS Applied Electronic Materials 2 4134–45
[15] Singh S, Lakshminarayana G, Sharma M, Dao T D, Chen K, Wada Y, Takeda T and Nagao T 2015 Excitation induced tunnel emission in Ce-Codoped BiPO4 Nanophosphors Journal of Spectroscopy 2015 493607
[16] Wang B, Ren Q, Bai O and Wu X 2017 Luminescence properties and energy transfer in Tb3+ and Eu3+ co-doped Ba2P2O7 phosphors RSC Adv. 7 15222–7
[17] Wang Y, Guo N, Shao B, Yao C, Ouyang R and Miao Y 2020 Adjustable photoluminescence of Bi3+ and Eu3+ in solid solution constructed by isostructural end components through composition and excitation-driven strategy Chem. Eng. J. 421 127735
[18] Wangkhem R, Yaba T, Singh N S and Nathgouham R S 2018 Red emission enhancement from CaMo2O4:Eu3+ by co-doping of Bi3+ for near UV/blue LED pumped white pcLEDs energy transfer studies J. Phys. Chem. 123 124303
[19] Min X, Huang Z, Fang M, Liu Y G, Tang C and Wu X 2014 Energy transfer from Sm3+ to Eu3+ in red-emitting phosphor LaMgAl2O4:Sm3+, Eu3+ for solar cells and near-ultraviolet white light-emitting diodes Inorg. Chem. 53 6060–5
[20] Bandi V R, Jayasimhadri M, Jeong J, Kang K and Jeong J H 2010 Host sensitized novel red phosphor CaZrSi2O7:Eu3+ for near UV and blue LED-based white LEDs J. Phys. D 43 395103
[21] Qiao J, Zhao J and Xiao Z 2019 A review on the Eu3+ doped β-Ca5(S4O10)2-type phosphors and the sites occupancy for photoluminescence tuning Optical Materials: X 1 100009
[22] Ai W, Wang X, Zou C, Du Z, Fan Z, Zhang H, Chen P, Yu T and Huang W 2017 Molecular-level design of hierarchically porous carbons coked with nitrogen and phosphorus capable of in situ self-activation for sustainable energy systems Small 13 162010
[23] Kaur S, Rao A S, Jayasimhadri M, Jaiswal V V and Haranath D 2020 Tb3+ ion induced colour tunability in calcium aluminozinicate phosphor for lighting and display devices J. Alloys Compd. 826 154212
[24] Zhao J, Dong J, Ye X and Wang L 2021 A promising novel red-emitting Eu3+-activated neodymium calcium phosphate phosphor with good thermal stability and excellent color purity for WLEDS J. Mol. Struct. 1240 130567
[25] Tran M T, Tu N, Quang N V, Nguyen D H, Thu L T H, Trung D Q and Huy P T 2021 Excellent thermal stability and high quantum efficiency orange-red-emitting AlPO4:Eu3+ phosphors for WLED application J. Alloys Compd. 853 156941
[26] Song E, Zhao W, Zhou G, Dou X, Yi C and Zhou M 2011 Luminescence properties of red phosphors Ca4La(Zr,P)2O12:Eu3+. J. Rare Earths 29 1340–3
[27] Hakeem D A and Park K 2015 Photoluminescence properties of red-emitting Ca5Sr3-x(P2O10)xEu3+ phosphors for white light-emitting diodes J. Nanosci. Nanotechnol. 15 5155–8
[28] Kosy K M et al 2018 Equation of state and amorphization of Ca4R(VO4)3 (R = La, Nd, Gd): a combined high-pressure x-ray diffraction and raman spectroscopy study Inorg. Chem. 57 13113–27
[29] Chen M, Xia Z, Molokoeve M S, Lin C C and Liu Q 2017 Probing Eu3+ luminescence from different crystallographic sites in Ca6M2(P2O7)3:Eu3+ (M = Li, Na, and K) with β-Ca5(S4O10)2-type structure Chem. Mater. 29 7563–70
Zhao F, Song Z and Liu Q 2021 Color-tunable persistent luminescence of Ca_{10}M(PO_4)_{7}:Eu^{2+} (M = Li, Na, and K) with a β-Ca_3(PO_4)_2-Type Structure. Inorg. Chem. 60 3952–60

Wang L, Xie R-I, Suehiro T, Takeda T and Hiroasaki N 2018 Down-conversion nitride materials for solid state lighting: recent advances and perspectives Chem. Rev. 118 1951–2009

Dorbakov N G, Titkov V V, Stefanovich S Y, Baryshnikova O V, Morozov V A, Belik A A and Lazoryak B I 2019 Barium-induced effects on structure and properties of β-Ca_3(PO_4)_2-type Ca_9Bi(VO_4)_7:Eu^{2+},Mn^{2+} with a β-Ca_3(PO_4)_2-Type Structure. Acta Mater. 79 6641–9

Huang C-H and Chen T-M 2010 Ca_9La(PO_4)_7:Eu^{2+},Mn^{2+}+: an emission-tunable phosphor through efficient energy transfer for white light-emitting diodes Opt. Express 18 5089–99

Dickens B 1974 Crystallographic studies of the role of Mg as a stabilizing impurity in β-Ca_3(PO_4)_2: I. The crystal structure of pure β-Ca_3(PO_4)_2. J. Solid State Chem. 10 232–48

Du F, Nakai Y, Tsuboi T, Huang and Seo H 2011 Luminescence properties and site occupations of Eu^{3+} ions doped in double phosphates Ca_9R(PO_4)_7 (R = Al, Lu). J. Mater. Chem. 21 4669–78

Tang M, Fan Y, Qiu Z, Zhan J, Yu L, Li C, Lian S and Zhou W 2017 Preparation, luminescence properties and energy transfer of Ca_9Y(PO_4)_7:Eu^{3+},Tb^{3+} phosphors J. Am. Ceram. Soc. 100 2991–9

Zhang J and Jiang C 2014 Photoluminescence properties of emission-tunable Ca_9MgLa(PO_4)_7:Eu^{2+}, Mn^{2+} phosphors for white LEDs Opt. Mater. Express 4 2102–7

Huang C-H, Wu P-J, Lee J-F and Chen T-M 2011 (Ca,Mg,Sr)_9Y(PO_4)_7:Eu^{2+},Mn^{2+}+: phosphors for white-light near-UV LEDs through crystal field tuning and energy transfer J. Mater. Chem. 21 10489–95

Kapustinskii A F 1956 Lattice energy of ionic crystals Q. Rev. Chem. Soc. 10 283–94

Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Physical Review B, Condensed Matter 54 11169

Kresse G and Furthmüller J 1996 Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set Comput. Mater. Sci. 6 15–50

Prasad V R, Babu S and Ratnakaram Y C 2016 Luminescence performance of Eu^{3+} doped lead free zinc phosphate glasses for red emission AIP Conf. Proc. 1728 020394

Wu L, Bai Y, Wu L, Yi H, Kong Y, Zhang Y and Xu J 2017 Sm^{3+} and Eu^{3+} codoped SrBi_2B_2O_7: a red-emitting phosphor with improved thermal stability RSC Adv. 7 1146–53

Zhao Y, Yang R, Wan W, Jing X, Wen T and Ye S 2020 Stabilizing CaPbBr_3 quantum dots with conjugated aromatic ligands and their regulated optical behaviors Chem. Eng. J. 389 124453

Tan C M, Singh P, Zhao W and Kuo H-C 2018 Physical limitations of phosphor layer thickness and concentration for white LEDs Sci. Rep. 8 24152