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Structure and luminescence properties of a novel broadband green-emitting oxyapatite-type phosphor

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In recent years, synthetic apatite-doped rare-earth luminescent materials and their optical properties have attracted extensive worldwide attention. In this study, a series of novel green phosphors Sr2Y3(SiO4)2(PO4)O:Eu2+ with apatite structure was fabricated via a high temperature solid-state reaction. X-ray diffraction, structure refinement, photoluminescence excitation, emission spectra, and temperature-dependent emission intensity were employed to describe the phase and property of the samples. Under the excitation of 365 nm, the phosphors emit strong green emission in the broad band range from 400 nm to 700 nm, which almost covers the visible light spectrum. The quenching concentration of Eu2+ in Sr2Y3(SiO4)2(PO4)O was about 0.05, which was attributed to the dipole–dipole interactions. The evidence that the as-prepared phosphor can be successfully excited by near ultraviolet light indicates that it can be potentially used as a near UV-convertible phosphor for white light-emitting diodes.

1. Introduction

It is well known that energy efficiency is one of the key parameters in illumination sources and other pervasive products. White light-emitting diodes (wLEDs) have bright future in traffic lights, displays, general lighting, and decorative lighting owing to their high efficiency and environment friendly nature.1–3 Currently, phosphor-converted wLEDs combining tricolor phosphors and near ultraviolet (n-UV) or blue chips have been extensively applied as solid-state lighting sources owing to their excellent performance and properties, e.g., long life, conversion efficiency, high color-rendering index, and lower power consumption.4–6

In general, a phosphor is composed of hosts and activators (sometimes sensitzers are also included).7 Rare-earth (RE) ions (Ce3+, Eu2+, and Tb3+) can be used as activators for white light-emitting diodes (wLEDs). The emission color changes when the RE ions are doped into different hosts derived from their 4f–4f or 4f–5d transitions.8 Eu2+ with a wide emission color range is a popular activator with intensive absorption in the UV and visible regions.9–14 Reactions between the ground state (4f energy level) and the excited 5d-state of Eu2+ can be influenced by the crystal lattice pattern, e.g., crystal-field strength, atom coordination, and covalence.15–17 Moreover, the careful selection of the host material is also critical since the host structure will affect the crystal field environment of the RE ions, which will change the energy transitions of the RE ions.18 A deeper understanding of the crystal structure of the targeted compound is necessary for choosing the host material because there are at least two or three suitable non-equivalent crystallographic sites for the Eu2+ occupation that can regulate the crystal field environment of Eu2+.19 Accordingly, efforts have been devoted for the development of novel host materials, containing abundant cationic crystallographic sites doped with Eu2+, which can be typically excited by n-UV light.20–23

The apatite-type structured compounds have two nonequivalent cationic sites for the Eu2+ occupation, which enables them to be one of the most potential phosphor host materials.24,25 In general, compounds with the apatite structure are characterized by a general chemical formula of M10[OX]6Y2, where M is defined as a divalent cation (Mg2+, Ca2+, Ba2+, etc.), whereas rare-earth ions (Y3+, La3+, Eu2+, etc.), alkali metal ions (Na+, K+, Ag+, etc.) can also enter the M-site, thus forming a coupling isomorphic substitution. [OX] is defined as a complex anionic group ([PO4]3−, [VO4]3−, [AsO4]3−, etc.), and Y commonly represents the anions such as F−, Br−, or OH−.26 In the past few decades, Eu2+-doped apatite phosphors have attracted considerable attention worldwide, e.g., Ca9(PO4)2F, Sr2(PO4)2Cl, Ca4Gd3(PO4)6O2, and Ca8Ba3(PO4)6Cl.28 However, no report is available on the Eu2+-doped Sr2Y3(SiO4)2(P2O7)2 phosphor with the apatite structure. On the other hand, developing novel apatite phosphors doped with Eu2+ that can be excited by n-UV light (350–420 nm) has a significant practical value.
Herein, a novel apatite-type phosphor $\text{Sr}_2\text{Y}_3\text{(SiO}_4\text{)}_2\text{(PO}_4\text{)}_2\text{O}:\text{Eu}^{2+}$, emitting green fluorescence, was successfully prepared via a high-temperature solid-state reaction. The crystal structure of the as-prepared sample was identified by the Rietveld refinement method in detail, which was used to study how the crystal structure and composition affected the luminescence property of the sample. In addition, the thermal luminescence property of the phosphor has also been revealed in this study. Under 365 nm excitation, the phosphor exhibits a strong green emission at 505 nm with an obvious band ranging from 400 nm to 700 nm, which almost covers the visible light spectrum. The results indicate that the $\text{Sr}_2\text{Y}_3\text{(SiO}_4\text{)}_2\text{(PO}_4\text{)}_2\text{O}:\text{Eu}^{2+}$ phosphor can act as a potential green phosphor for n-UV phosphor-converted wLEDs.

2. Experimental procedure

2.1. Materials and synthesis

The $\text{Sr}_2\text{Y}_3\text{(SiO}_4\text{)}_2\text{(PO}_4\text{)}_2\text{O}:\text{Eu}^{2+}$ phosphor was synthesized using the traditional high-temperature solid-phase synthesis method with starting materials, including SrCO$_3$ (Aldrich, 99.9%), Y$_2$O$_3$ (Aldrich, 99.99%), NH$_4$H$_2$PO$_4$ (Aldrich, 99.9%), SiO$_2$ (Aldrich, 99.99%), and Eu$_2$O$_3$ (Aldrich, 99.99%). First, they were weighed in an electronic balance according to the stoichiometric ratio. Then, they were mixed and ground thoroughly in an agate mortar. Further, the raw materials were preheated at 500 °C for 3 h in a furnace and moved into alumina crucibles after being cooled down to room temperature. In addition, the preliminary products were annealed at 1400 °C for 5 h under a reducing atmosphere (10% H$_2$ + 90% N$_2$). When the furnace was cooled down to room temperature again, the final product was smashed and re-ground for subsequent tests.

2.2. Characterization

The phase structure of each sample was evaluated using an X-ray powder diffractometer (RigakuDmax 12 kW, Japan) with Cu Kα radiation ($λ = 0.15418$ nm) from 10° to 70° (2θ). The Rietveld refinement of $\text{Sr}_2\text{Y}_3\text{(SiO}_4\text{)}_2\text{(PO}_4\text{)}_2\text{O}:\text{Eu}^{2+}$ was carried out by the TOPAS software. Photoluminescence and excitation spectra of the sample were recorded using a fluorescence spectrophotometer (FL-4600, HITACHI, Japan) fitted with a 700 V and 150 W Xe lamp source. Lifetime of the samples was tested using a spectrometer (HORIBA JOBIN YVON FL3-21) with excitation by a pulsed radiation laser at 370 nm.

3. Results and discussions

Fig. 1 presents the XRD patterns of $\text{Sr}_{2−x}\text{Eu}_x\text{(SiO}_4\text{)}_2\text{(PO}_4\text{)}_2\text{O}:\text{Eu}^{2+}$ ($x = 0.01$ and 0.05) and the referred standard data for $\text{Ca}_8\text{Nd}_2\text{(PO}_4\text{)}_6\text{O}_2$ (PDF-32-175-Ca$_8$Nd$_2$(PO$_4$)$_6$O$_2$) is shown as a reference. To further investigate the phase purity and occupation of Eu$^{2+}$, TOPAS 4.2 (ref. 31) was used to analyze the Rietveld refinement. The structure of $\text{Ca}_8\text{Nd}_2\text{(PO}_4\text{)}_6\text{O}_2$, possessing a hexagonal structure with the space group $P6_3/m$, was employed as the initial model. Silicon oxygen tetrahedron and phosphorus oxygen tetrahedron is independent with each other Sr1 and Sr2 occupy two independent sites for Sr$^{2+}$ in the crystal lattice. Sr1 is in a 9-fold coordination state, and Sr2 is in a 7-fold coordination state. Similar to Sr$^{2+}$, the radii of Eu$^{2+}$ in the 7-fold coordination and 9-fold coordination sites are 0.120 and 0.130 nm, respectively. Eu$^{2+}$ can occupy the two positions of Sr$^{2+}$. The Rietveld analysis patterns for the X-ray power diffraction data of $\text{Sr}_{3.95}\text{Eu}_0.05\text{(SiO}_4\text{)}_2\text{(PO}_4\text{)}_2\text{O}_2$ is shown in Fig. 2. The occupation of the cations was set to a fixed value according the chemical formula. The fractional atomic coordinates, isotropic displacement parameters, and the cell parameters were refined. The atomic coordinates, occupancies and

![Fig. 1](image1.png)

![Fig. 2](image2.png)
displacement parameters (Å²) are listed in Table 1, and the cell parameters and reliability factors are listed in Table 2. The cell parameters are $a = b = 9.477(10)$ Å, $c = 6.954(80)$ Å, $a = 90^\circ$, $b = 90^\circ$, $c = 6.954(80)$ Å, $a = 90^\circ$, $b = 90^\circ$, and $c = 6.954(80)$ Å. The refinement was stable and the fit is convincing with low $R$-factors, which verify the phase purity of the as-prepared sample.

The photoluminescence excitation and emission spectra of the Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:0.05Eu$^{2+}$ are given in Fig. 3(a). It is clear that the PLE spectrum has an absorption band at 274 nm, which resulted from the 4f–5d transitions in Eu$^{2+}$. The PL spectrum exhibits a green emission peak at 505 nm, which can be decomposed into two sub-bands with Gaussian fitting at 498 nm and 555 nm, respectively (Fig. 3(b)). Therefore, Eu$^{2+}$ can occupy two cationic lattices, which is consistent with the refined results. The lattice site centers of Eu$^{2+}$ can be determined using the van Uitert empirical equation:

$$E = Q \left[ 1 - \left( \frac{V}{4} \right)^{\frac{1}{3}} \right] \left[ \frac{n \cdot E_a \cdot t}{V^2} \right]$$

where $E$ is the position of the low-energy of the 5f excited-state (cm$^{-1}$) or the emission peak of Eu$^{2+}$, $Q$ is $34,000$ cm$^{-1}$, $V$ is 2, $n$ is the anion number around Eu$^{2+}$, $E_a$ is a constant, $r$ is the effective radius of Sr$^{2+}$ (nm). Therefore, $E$ is negatively correlated with $n$.

Two different luminescent centers, having nine and seven coordinations, contribute to the fluorescence emission peaks at 498 and 555 nm, respectively.

![Fig. 3](a) Excitation and emission spectra of the Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:0.05Eu$^{2+}$ sample, (b) PL spectrum of Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:0.05Eu$^{2+}$ excited at 365 nm and Gaussian fitting result. Two Gaussian components are peaked at 498 nm and 555 nm.
quenching mechanism, the critical energy transfer distance $R_C$ can be calculated first:\textsuperscript{34}

\begin{equation}
R_C \approx 2 \left[ \frac{3V}{4\pi \chi_c N} \right]^{\frac{1}{3}}
\end{equation}

(2)

For the host with $x_C = 0.05$, $V = 540.53$ Å$^3$, $N = 10$, the obtained critical distance $R_C$ is $12.74$ Å. According to Dexter theory, when the $R_C$ value is >5, a non-radiative transition occurs between the Eu$^{2+}$ ions; therefore, the type of energy transfer can be described as follows:\textsuperscript{35,36}

\begin{equation}
I_x = K \left[ 1 + \beta(x)^{\frac{1}{\theta}} \right]^{-\frac{1}{\theta}}
\end{equation}

(3)

where $I$ is the emission intensity and $x$ is the activator concentration of Eu$^{2+}$, $\theta = 6$, 8, and 10 for dipole–dipole (d–d), dipole–quadrupole (d–q), and quadrupole–quadrupole (q–q), respectively.\textsuperscript{37,38} Fig. 4(c) shows the relational curve between log($I/x$) and log($x$) in the Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:0.05Eu$^{2+}$ phosphors under the 365 nm light irradiation with line slope of $-2.085$, and the calculated $\theta$ value based on eqn (3) is 6.255, which means that the concentration quenching mechanism of Eu$^{2+}$ in the sample is d–d.

The PL decay curve of the Eu$^{2+}$ phosphor was detected at 365 nm, which can be used to determine the fluorescence lifetime. Fig. 5 describes the decay curves of the phosphor, which can be fitted by a double-exponential equation:\textsuperscript{39,40}

\begin{equation}
I = A_1 \exp \left( -\frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right) + I_0
\end{equation}

(4)

where $I_0$ is the initial emission intensity, $t$ represents time, $A_1$ and $A_2$ are invariant constants after fitting, and $\tau_1$ and $\tau_2$ are two different decay lives. The calculated Eu$^{2+}$ lifetime is 0.613 µs.

The variable temperature fluorescence test was carried out to show the thermal stability of the sample. Fig. 6(a) presents the relationship between the emitted light color and the ambient temperature in the wavelength range from 400 to 700 nm. As shown in Fig. 6(b), the emission intensity of the sample is 63% of that at room temperature with the temperature rising to $150$ °C, indicating an excellent thermal stability. In addition, the strongest emission peak moves from 502 to 490 nm. The emission band has slight blue shift with an increase in temperature. The activation energy ($E$) can be obtained by the Arrhenius equation:\textsuperscript{41,42}

\begin{equation}
\ln \left( \frac{I_0}{I} \right) = \ln A - \left( \frac{E}{kT} \right)
\end{equation}

(5)

where $I(0)$ is the initial emission intensity of the phosphor at 25 °C and $I(T)$ is the emission intensity at different temperatures, $c$ is constant, $E$ is the activation energy for thermal quenching, and $k$ is the Boltzmann constant ($8.617 \times 10^{-5}$ eV). The plot of $\ln[I(0)/I]^{-1}$ vs. $1/kT$ in Fig. 6(c) follows a line trend, obtaining 0.210 eV as the activation energy $E$. Fig. 6(d) shows that the calculated CIE chromaticity coordinates of Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:0.05Eu$^{2+}$ is (0.233, 0.446), and the green

**Fig. 4** (a) PL spectra of Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:xEu$^{2+}$ ($x = 0.01, 0.03, 0.05, 0.07, 0.09$, and 0.12) under the excitation of 365 nm, (b) intensities of Eu$^{2+}$ as a function of Eu$^{2+}$ doping concentration, and (c) linear fitting of log($x$) versus log($I/x$) in the Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:0.05Eu$^{2+}$ samples.

**Fig. 5** Decay curves of Eu$^{2+}$ in the Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:0.05Eu$^{2+}$ phosphor.
emission can be observed clearly from the image of Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:0.05Eu$^{2+}$ at ultraviolet excitation.

4. Conclusions

A series of green phosphors Sr$_2$Y$_3$(SiO$_4$)$_2$(PO$_4$)O$_2$:Eu$^{2+}$ with apatite structure were successfully synthesized via a traditional high-temperature solid-phase reaction and their luminescent properties were investigated. The phosphors generated a strong green emission band at 505 nm with an obvious broad band ranging from 400 to 700 nm. The determined optimal Eu$^{2+}$ concentration of Sr$_2$Y$_3$(SiO$_4$)$_2$(PO$_4$)O$_2$:Eu$^{2+}$ is 0.05. The experimental results and theoretical calculations suggest that the concentration quenching mechanism of Eu$^{2+}$ in the Sr$_{3.95}$Y$_6$(SiO$_4$)$_4$(PO$_4$)$_2$O$_2$:0.05Eu$^{2+}$ phosphor is d–d and the decay time of it was around 0.613 μs. All the investigations show that the as-prepared phosphor can be a green phosphor having potential research value.

Conflicts of interest

There are no conflicts to declare.

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References

1 R. P. Cao, Y. L. Cao, T. Fu, S. H. Jiang, W. S. Li, Z. Y. Luo and J. W. Fu, Synthesis and luminescence properties of novel red-emitting R$_2$P$_6$O$_{13}$Bi$^{2+}$ (R = Sr and Ba) phosphors, J. Alloys Compd., 2016, 661, 77–81.

2 L. Li, X. H. Tang, Z. Q. Jiang, X. J. Zhou, S. Jiang, X. B. Luo, G. T. Xiang and K. N. Zhou, NaBaLa$_2$(PO$_4$)$_3$: A novel host lattice for Sm$^{3+}$-doped phosphor materials emitting reddish-orange light, J. Alloys Compd., 2017, 701, 515–523.

3 R. P. Cao, C. L. Liao, F. Xiao, G. T. Zheng, W. Hu, Y. M. Guo and Y. X. Ye, Emission enhancement of LiLaMo$_2$O$_8$:Eu$^{3+}$ phosphor by co-doping with Bi$^{3+}$ and Sm$^{3+}$ ions, Dyes Pigm., 2018, 149, 574–580.

4 M. Runowski, S. Goderski, J. Paczesny, M. Ksiezopolska-Gocałka, A. Ekner-Grzyb, T. Grzyb, J. D. Rybka and M. Giersig, Stefan Lis Preparation of Biocompatible, Luminescent-Plasmonic Core/Shell Nanomaterials Based on Lanthaneide and Gold Nanoparticles Exhibiting SERS Effects, J. Phys. Chem. C, 2016, 120, 23788–23798.
5 W. Wang, H. Yang, Y. X. Liu, X. X. Liu, X. H. Yun, Y. Wei and G. G. Liu, (Ln3+ = Ce3+, Eu3+)-doped oxypatite-type phosphors, CrystEngComm, 2020, 22, 319–320.

6 B. Han, Y. Z. Dai, J. Zhang, B. B. Liu and H. Z. Shi, Development of near-ultraviolet-excitable single-phase white-light-emitting phosphor KBa5Y(BO3)3:Ce3+, Dy3+ for phosphor-converted white light-emitting diodes, Ceram. Int., 2010, 36, 1–34.

7 M. Runowski and S. Lis, Preparation and photophysical properties of luminescent nanoparticles based on lanthanide doped fluorides (LaF3:Ce3+, Gd3+, Eu3+), obtained in the presence of different surfactants, J. Alloys Compd., 2014, 597, 63–71.

8 P. Du, W. G. Ran, W. P. Li, L. H. Luo and X. Y. Huang, Morphology evolution of Eu3+-activated NaTbF4 nanorods: a highly-efficient near-ultraviolet light-triggered red-emitting platform towards application in white light-emitting diodes, RSC Adv., 2019, 7, 10802–10809.

9 Q. Y. Bai, Z. J. Wang, P. L. Li, S. C. Xu, T. Li and Z. P. Yang, Zn3−aGeO2+aRE and Zn2Ge1−aO2RE (RE = Ce3+, Eu3+, Tb3+, Dy3+): 4f–4f and 5d–4f transition luminescence of rare earth ions under different substitution, RSC Adv., 2016, 6, 102183–102192.

10 W. J. Tang, Z. X. Huang and J. X. Liang, Controllable luminescence in Eu2+-doped Li3Sr4Al[PO4]3 phosphor via tuning the Eu3+ concentration and codoping Ce3+, J. Alloys Compd., 2019, 778, 612–617.

11 H. R. Li, Y. J. Liang, Y. L. Zhu, S. Q. Liu, J. H. Chen, H. Zhang and Y. J. Chen, Investigation of local structure distortion and electron cloud interaction on emission-band broadening induced by the concentration perturbation effect of cation substitution in Ba1.95Y2.05(SiO4)3F:Eu3+ phosphors, CrystEngComm, 2019, 21, 4771–4785.

12 Q. Zhang, X. Ding and Y. H. Wang, Novel highly efficient blue-emitting SrHfSiO5:Eu2+ phosphor: a potential color converter for WLEDs and FEDs, Dyes Pigm., 2019, 163, 168–175.

13 S. S. Lin, H. Lin, Q. M. Huang, Y. Cheng, J. Xu, J. M. Wang, X. Q. Xiang, C. Y. Wang, L. Q. Zhang and Y. S. Wang, Optical Storage: A Photostimulated BaSi2O5:Eu2+, Nd3+ Phosphor-in-Glass for Erasable-ReWritable Optical Storage Medium, Laser Photonics Rev., 2019, 13(4), 1863–8880.

14 M. Fei, Y. F. Tian, Z. Zhang, L. R. He, J. Chen, F. D. Bao, P. J. Zhang, Q. H. Zhang and L. Chen, The competitive mechanisms of nano-SiO2 and reaction temperature on phase transformation and Eu2+ site occupation in Sr5SiO4:Eu2+ phosphor, J. Alloys Compd., 2017, 728, 231–240.

15 S. A. Khan, H. Zhong, W. W. Ji, N. Z. Khan, H. Abadikhah, L. Y. Hao, X. Xu, S. Agathopoulos and Q. L. Bao, Crystal-site engineering for developing tunable green light emitting Ba4La5Si6O24:Eu2+ phosphors for efficient white LEDs, J. Alloys Compd., 2018, 767, 374–381.

16 A. M. I. Ibrahim, Structural, electronic and optical properties of prominent M3Si4N5Eu2+ phosphors (M = Mg, Ca, Sr, Ba) from the ground-state and excited-state first principles calculations, J. Alloys Compd., 2019, 775, 30–38.

17 X. G. Zhang, F. W. Mo, Z. P. Zhu and Z. Y. Guo, Structure, site-occupancy and luminescence properties of a novel blue phosphor Na3ZrMg2PO12:Eu5+, Mater. Res. Bull., 2018, 106, 396–402.

18 P. Dorenbos, A Review on How Lanthanide Impurity Levels Change with Chemistry and Structure of Inorganic Compounds, ECS J. Solid State Sci. Technol., 2013, 2, R3001–R3011.

19 H. G. Guo, Y. H. Wang, G. Li, J. Y. Liu and Y. Y. Li, The persistent energy transfer of Eu2+ and Dy3+ and luminescence properties of a new cyan afterglow phosphor alpha-Ca3(PO4)2:Eu2+, Dy3+, RSC Adv., 2016, 6, 101731–101736.

20 X. C. Wang, Z. Y. Zhao, Q. S. Wu, Y. Y. Li, C. Wang, A. J. Mao and Y. H. Wang, Synthesis, structure, and luminescence properties of Sr3Al2O4:N2:Eu2+ phosphors for light-emitting devices and field emission displays, Dalton Trans., 2015, 44, 11057–11066.

21 X. X. Ma, L. F. Mei, H. K. Liu, L. B. Liao, K. Nie, Y. Q. Liu and Z. H. Li, Synthesis and luminescence properties of Eu2+-activated phosphor Ba5LaK[PO4]3F for n-UV white-LEDs, Polyhedron, 2016, 119, 223–226.

22 G. Li, Y. H. Wang, D. W. Liu, H. J. Guo and J. Liu, Cyan longlasting phosphorescence in green emitting phosphors Ba2GdSi4O12:Eu2+, RE3+ (RE = Dy3+, Ho3+, Tm3+, Nd3+ and Tb3+), RSC Adv., 2016, 6, 7024–7032.

23 S. M. Xu, K. Tang, T. Han, L. L. Luo and D. C. Zhu, Effect of Eu2+ on the luminescence properties of Ba1.52Zn0.38Li0.4SiO4:0.05Ce3+, 0.03Mn2+, xEu2+ phosphor, Optik, 2016, 127, 2370–2373.

24 B. Deng, J. Chen, H. Liu and C. S. Zhou, Photoluminescence properties of dysprosium doped novel apatite-type Ba2Y3(SiO4)3F white-emitting phosphor, J. Mater. Sci.: Mater. Electron., 2019, 30, 7507–7513.

25 N. Guo, C. Z. J. Jia, Y. F. Zhao, R. Z. Ouyang and W. Lu, White-Emitting Tuning and Energy Transfer in Eu2+/Mn2+. Substituted Apatite-Type Fluorophosphate Phosphors, J. Am. Ceram. Soc., 2015, 98, 1162–1168.

26 J. R. Peet, A. Piovano, M. R. Johnson and I. Radosavljevic Evans, Location and orientation of lone pairs in apatite-type materials: a computational study, Dalton Trans., 2015, 44, 1162–1168.

27 W. J. Tang and F. Zhang, A Single-Phase Emission-Tunable Ca5(PO4)2:F:Eu2+,Mn2+ Phosphor with Efficient Energy Transfer for White LEDs, Eur. J. Inorg. Chem., 2014, 21, 3387–3392.

28 S. J. Dhoble, Preparation and characterization of the Sr3(PO4)2:Cl:Eu2+ phosphor, J. Phys. D: Appl. Phys., 2000, 33(2), 158–161.

29 G. Seeta Rama Raju, J. Y. Park, G. P. Nagaraju, E. Pavitra, H. K. Yang, B. K. Moon, J. S. Yu, Y. S. Huh and J. H. Jeong, Evolution of CaGd2ZnO5:Eu3+ nanostructures for rapid visualization of latent fingerprints(Article), J. Mater. Chem. C, 2017, 5, 4246–4256.

30 M. M. Shang, D. L. Geng, D. M. Yang, X. J. Kang, Y. Zhang and J. Lin, Luminescence and Energy Transfer Properties of Ca3Ba3(PO4)2Cl and Ca3Ba3(PO4)2ClA (A = Eu2+/Ce3+/
Dy\textsuperscript{3+}/Tb\textsuperscript{3+}) under UV and Low-Voltage Electron Beam Excitation, \textit{Inorg. Chem.}, 2013, 52, 3102–3112.

31 Bruker AXS, \textit{TOPAS V4: General Profile and Structure Analysis Software for Powder Diffraction Data – User’s Manual}, Bruker AXS, Karlsruhe, Germany, 2008.

32 Y. Z. Fang, F. X. Liu, J. S. Hou, Y. Zhang, X. F. Zheng, N. Zhang, G. Y. Zhao, M. S. Liao, G. Z. Dai, M. Q. Long and Y. F. Liu, Photoluminescence properties of blue light excited Ca\textsubscript{8}La\textsubscript{2}(PO\textsubscript{4})\textsubscript{6}O\textsubscript{2}:Eu\textsuperscript{3+} red phosphors, \textit{J. Lumin.}, 2016, 177, 280–2885.

33 L. G. van Uitert, An empirical relation fitting the position in energy of the lower d-band edge for Eu\textsuperscript{2+} OR Ce\textsuperscript{3+} in various compounds, \textit{J. Lumin.}, 1984, 29, 1–9.

34 G. Blasse, Energy transfer in oxidge phosphors, \textit{Phys. Lett. A}, 1968, 28, 444–445.

35 J. Y. Sun, X. Y. Zhang, Z. G. Xia and H. Y. Du, Synthesis and luminescence properties of novel LiSrPO\textsubscript{4}:Dy\textsuperscript{3+} phosphor, \textit{Mater. Res. Bull.}, 2011, 46, 2179–2182.

36 L. M. Liang, L. F. Mei, H. K. Liu, C. C. Wang and L. B. Liao, Intense broad-band absorption and blue-emitting Ca\textsubscript{8}La(PO\textsubscript{4})\textsubscript{6}(SiO\textsubscript{4})\textsubscript{2}:Eu\textsuperscript{2+} phosphor under near-ultraviolet excitation, \textit{J. Lumin.}, 2019, 206, 154–157.

37 Q. F. Guo, B. Ma, L. B. Liao, M. S. Molokeev, L. F. Mei and H. K. Liu, Crystal structure and luminescence properties of novel Sr\textsubscript{10–x}(SiO\textsubscript{4})\textsubscript{3}(SO\textsubscript{4})\textsubscript{3}O\textsubscript{x}:Eu\textsuperscript{2+} phosphor with apatite structure, \textit{Ceram. Int.}, 2016, 42, 11687–11691.

38 H. K. Liu, Y. Y. Zhang, L. B. Liao, Q. F. Guo and L. F. Mei, Synthesis, broad-band absorption and luminescence properties of blue-emitting phosphor Sr\textsubscript{4}La\textsubscript{3}(PO\textsubscript{4})\textsubscript{6}O\textsubscript{2}:Eu\textsuperscript{2+} for n-UV white-light-emitting diodes, \textit{Ceram. Int.}, 2014, 40, 13709–13713.

39 B. Ramesha, G. Devarajulua, B. Deva Prasad Rajub, G. BhaskarKumarc, G. R. Dillipd, A. N. Banerjeed and S. W. Jood, Determination of strain, site occupancy, photoluminescent, and thermoluminescent-trapping parameters of Sm\textsuperscript{3+}-doped NaSrB\textsubscript{2}O\textsubscript{4} microstructures, \textit{Ceram. Int.}, 2016, 42, 1234–1245.

40 H. Ye, M. Y. He, T. S. Zhou, Q. F. Guo, J. L. Zhang, L. B. Liao, L. F. Mei, H. K. Liu and M. Runowski, A novel reddish-orange fluorapatite phosphor, La\textsubscript{x–z}Ba\textsubscript{z}(SiO\textsubscript{4})\textsubscript{6}F\textsubscript{2}:xSm\textsuperscript{3+} - Structure, luminescence and energy transfer properties, \textit{J. Alloys Compd.}, 2018, 757, 79–86.

41 S. Arrhenius, Über Die Reaktionsgeschwindigkeitbei der Inversion von RohrzuckerDurchSäuren, \textit{Z. Phys. Chem.}, 1889, 4, 226–248.

42 J. W. Qiao, L. X. Ning, M. S. Molokeev, Y. C. Chuang, Q. L. Liu and Z. Xia, Eu\textsuperscript{2+} site preferences in the mixed cationK\textsubscript{2}BaCa(PO\textsubscript{4})\textsubscript{2} and thermally stable luminescence, \textit{J. Am. Chem. Soc.}, 2018, 140, 9730–9736.