Single-Phase White Light-Emitting $\text{Ca}_x\text{Ba}_{(9-x)}\text{Lu}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}/\text{Mn}^{2+}$ Phosphors

Sayed Ali Khan, † Hao Zhong, † Weiwei Ji, † Lu-Yuan Hao, † Hamidreza Abadikhah, † Xin Xu, * ‡ Xu Noor Zamin Khan, † and Simeon Agathopoulos§

† Chinese Academy of Science, Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, and § Key Laboratory of Quantum Information, School of Physical Sciences, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

ABSTRACT: Single-phase white light-emitting $\text{Ca}_x\text{Ba}_{(9-x)}\text{Lu}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}/\text{Mn}^{2+}$ codoped phosphors were successfully synthesized, and their photoluminescence properties were experimentally determined. The analysis of the experimental results suggests that the partial substitution of $\text{Ba}^{2+}$ ions by smaller $\text{Ca}^{2+}$ ions alters the distribution of the $\text{Eu}^{2+}$ luminescence center among the three available $\text{Ba}^{2+}$ sites in the host lattice, which enables the emission to be efficiently tuned from blue to blue-green-yellow region. The incorporation of $\text{Mn}^{2+}$ ions resulted in a red light emission at around 618 nm, through energy transfer from $\text{Eu}^{2+}$ to $\text{Mn}^{2+}$ ions via dipole–dipole interactions. The incorporation of $\text{Ca}^{2+}$ and $\text{Mn}^{2+}$ ions also resulted in improved thermal stability. The results qualify the produced $\text{Ca}_x\text{Ba}_{(9-x)}\text{Lu}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}/\text{Mn}^{2+}$ composition as a potential ultraviolet-convertible white light-emitting phosphor.

1. INTRODUCTION

White light-emitting diodes (WLEDs) are environmentally friendly materials and exhibit outstanding characteristics, such as high efficiency, long lifetime, low energy consumption, and high reliability. Phosphors are indispensable components in WLEDs because they have a strong contribution to their color index and efficiency.1–5

However, in various types of phosphor-converted WLED systems, the combination of the blue LED chip with yellow YAG:Ce³⁺ phosphors6 does not provide the desired quality of color of WLEDs because of the poor color rendering index (CRI, $R_c < 80$), which is due to the lack of red and green light contributions.6–8 Therefore, the blue LED chip and yellow-emitting phosphors with a wider spectral coverage in the green/red region or UV LED (380–420 nm), and red, green, and blue multicomponent phosphors are combined to achieve high-quality white light with a high CRI ($R_c > 80$).2–5,6–11 Nevertheless, the resultant materials still display poor luminescence efficiency, attributed to reabsorption phenomena. Accordingly, there is a strong interest in developing highly efficient phosphors with a tunable color in the entire visible region under blue or UV light excitation, which must also feature high thermal quenching temperatures. It is also worthy to note that the use of single-phase white light phosphors (instead of multicomponent phosphors) should efficiently improve white LEDs because they can limit some variations in the phosphors blend.12–19 The latter approach can eventually allow the adjustment and control of the emission in complementary color regions by a simple mixing method to obtain white light.

In the case of more than one cation sites being present at the host lattice, the activator ion can preferentially enter the most appropriate site on account of a possible mismatch between the activator ion and the host cation at a specific site.20 This means that the luminescence in such a multication host may shift toward longer wavelength (and thus effective tuning can be achieved) by increasing the concentration of doping ions, for example, in Sr₂SiO₄:Eu²⁺ the increase in the concentration of doping ions will be forced to enter less appropriate sites in the host,21–24 yet, the increase in the concentration of doping ions can cause luminescence quenching. Moreover, modification in the preferred cation site can also force the luminescence center to distribute among the available cation sites in a multication host.20,25–29 For instance, in Sr₂SiO₄:Eu²⁺ phosphors, more Eu²⁺ ions can occupy Sr(II) sites and result in emission at a long wavelength.24

A typical example is the $\text{Ba}_9\text{Lu}_2\text{Si}_6\text{O}_{24}$ (BLSO) host, which crystallizes in the rhombohedral structure and belongs to the R3(148) space group ($a = b = 9.9905$, $c = 22.1088$, and $V = 1911.04$), as shown in Figure 1.30,31 There are three different and independent Ba²⁺ crystallographic sites, which are the 12 coordinated Ba(1) sites, the 9 coordinated Ba(2) sites, and the 10 coordinated Ba(3) sites with average bond lengths of 3.085 Å (Ba(1)−O, 2.925 Å (Ba(2)−O), and 2.934 Å (Ba(3)−O). The Eu²⁺-doped $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}$ and $\text{Ba}_9\text{Y}_2\text{Si}_6\text{O}_{24}$ phosphors emit efficient green light under UV and near-UV light irradi-
The efficient green light emission along with their respective excitation can be adjusted with substitution of Sr\(^{2+}\) for Ba\(^{2+}\). On the other hand, the Eu\(^{2+}\)-doped BLSO phosphor emits blue light (462 nm) under UV light irradiation (343 nm), as compared to the green light emission of the aforementioned Eu\(^{2+}\)-doped Ba\(_9\)Sc\(_2\)Si\(_6\)O\(_{24}\) and Ba\(_9\)Y\(_2\)Si\(_6\)O\(_{24}\) phosphors. Nonetheless, there is still poor documentation on this difference, that is, between the blue light emission in the Eu\(^{2+}\)-doped BLSO phosphor and the green light emission of Ba\(_9\)Sc\(_2\)Si\(_6\)O\(_{24}\) and Ba\(_9\)Y\(_2\)Si\(_6\)O\(_{24}\) phosphors, considering that all of them have the same crystalline structure. The coordination environment of the luminescence center is unequivocally a crucial factor in determining the luminescence properties of activator ions. Therefore, the BLSO structure offers a potentially wide range of possibilities as far as the occupation of luminescence ions is concerned.

The primary aim of the present study is to shed light on the origin of the blue light emission of BLSO:Eu\(^{2+}\) phosphors. Also, efficient modifications were attempted to cover the full spectrum of white light. More specifically, the substitution of smaller Ca\(^{2+}\) ions for larger Ba\(^{2+}\) ions aimed for a photoluminescence (PL) emission that can cover the blue and the green region. Then, the addition of Mn\(^{2+}\) ions, as coactivators, aimed at expanding the emission spectrum in the red region, owing to efficient energy transfer from Eu\(^{2+}\) to Mn\(^{2+}\). The related properties, such as PL, stability against temperature, energy-transfer efficiency, decay time, and CRI values, were thoroughly investigated.

2. RESULTS AND DISCUSSION

2.1. Crystalline Structure. The influence of Ca and Mn substitutions on the crystalline structure of the produced Ca\(_x\)Ba\(_{8.8-x}\)Lu\(_2\)Si\(_6\)O\(_{24}\):0.2Eu\(^{2+}\) (for \(x = 0, 0.3, 0.6, 0.9, 1.2, 1.5, \) and 1.8) and Ca\(_{1.5}\)Ba\(_{7.38-y}\)Lu\(_2\)Si\(_6\)O\(_{24}\):0.12Eu\(^{2+}\)/yMn\(^{2+}\) (for \(y = 0, 0.1, 0.3, 0.5, 0.7, 0.9, \) and 1) phosphors is presented in the diffractograms of Figures 2 and 3, respectively. In all cases, the phase of BLSO (whose X-ray standard diffraction patterns are plotted at the bottom of the diagrams) was exclusively identified. The increase of the substitution of Ca\(^{2+}\) and Mn\(^{2+}\) for Ba\(^{2+}\) ions in the host lattice merely caused a slight shift of the peaks toward higher angles, as clearly seen in the magnified plots in the region between 30° and 31° at the right-hand side of the diagrams. This shift suggests a slight shrinkage of the host lattice, ascribed to the difference in the ionic radii: they are 100 nm for Ca\(^{2+}\) and 67 nm for Mn\(^{2+}\), which are smaller than that of Ba\(^{2+}\) (135 nm).

2.2. Influence of Ca Substitution on the PL Properties. The influence of the substitution of Ca\(^{2+}\) ions for Ba\(^{2+}\) ions in the BLSO host on the PL properties of BLSO phosphors (which actually occurred because of the Eu\(^{2+}\) ions) was investigated. To obtain a better perspective of the influence of this substitution, both the nonnormalized and the normalized excitation (photoluminescence excitation, PLE) and emission (PL) spectra of Ca\(_{1.5}\)Ba\(_{7.38-y}\)Lu\(_2\)Si\(_6\)O\(_{24}\):0.12Eu\(^{2+}\)/yMn\(^{2+}\) phosphors for \(x = 0, 0.3, 0.6, 0.9, 1.2, 1.5, \) and 1.8 are presented in the right-hand side. The X-ray standard patterns of BLSO are also plotted.
The PLE band (Figure 4a) was recorded between 200 and 450 nm, with maximum peaks at 318 and 343 nm. This broad band, which can be attributed to the $4f^7 \rightarrow 4f^65d^1$ electric dipole allowed transition of Eu$^{2+}$, suggests that the CBLSO phosphors (where C stands for Ca) can be efficiently excited by both a UV and a near-UV chip in WLED applications.

An intense blue light emission was recorded with the Ca-free BLSO:0.2Eu$^{2+}$ phosphor between 400 and 700 nm, with a peak at 462 nm, under excitation at 343 nm UV light (Figure 4b). The deconvolution of this emission band (bottom diagram in Figure 4c) resulted in three Gaussian components with peaks at 465, 496, and 573 nm. This suggests that there are three different types of luminescence centers in the BLSO host lattice, which should be correlated to the three different Ba$^{2+}$ sites, as described in the Introduction section. According to the values reported there and in Figure 1, the average Ba–O bond length is similar for the Ba(2) and Ba(3) sites and shorter than the bond length of the Ba(1) site. This means that a stronger crystal field strength is provided, and a nephelauxetic effect on the 5d orbital of Eu$^{2+}$ occurs in the Ba(2) and Ba(3) sites. The position of the lowest 5d level for Eu$^{2+}$ ions in an inorganic host is dependent on the crystal field splitting of the 5d energy level, and the crystal field strength is inversely proportional to the distance from the coordinate ligands to the central cation. Thus, the higher energy blue light emission peak at 465 nm can be ascribed to the preferential occupation of Eu$^{2+}$ ions in the most loose Ba(1) sites, whereas the lower energy peaks at 496 and 573 nm are due to the occupation of Eu$^{2+}$ ions in Ba(3) and Ba(2) sites.

Emission spectra expand into a longer wavelength when Ca$^{2+}$ ions progressively replace Ba$^{2+}$ ions (Figure 4b, for $x > 0$) and cover both the blue and the green regions of white light. This also gradually changes the relative proportion of the intensity of the three components mentioned above, and the bands with peaks at 496 and 573 nm are intensified (upper plot in Figure 4c). These results suggest that the substitution of Ca$^{2+}$ for Ba$^{2+}$ ions causes a movement of Eu$^{2+}$ ions from Ba(1) sites to Ba(3) and Ba(2) sites, apparently because the Ca$^{2+}$ ions have smaller ionic radii than both Eu$^{2+}$ ions and Ba$^{2+}$ ions. Hence, Ca$^{2+}$ ions occupy the Ba(1) sites, which leads the Eu$^{2+}$ ions to occupy Ba(3) and Ba(2) sites.$^{37}$
2.3. \( \text{Ca}_{1.5}\text{Ba}_{7.5}\text{Lu}_2\text{Si}_6\text{O}_{24}:0.12\text{Eu}^{2+}/y\text{Mn}^{2+} \) Phosphors.

2.3.1. Luminescence Properties. The above results showed that the increase in the content of \( \text{Ca}^{2+} \) ions in \( \text{Ca}_{x}\text{Ba}_{(9-x)}\text{Lu}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+} \) phosphors broadened the emission spectra (Figure 4) in a way that they covered both the blue and the green regions, which can produce nearly white light. Therefore, the next step was to introduce red-emitting \( \text{Mn}^{2+} \) ions into the optimum sample, which was the \( \text{Ca}_{1.5}\text{Ba}_{7.5}\text{Lu}_2\text{Si}_6\text{O}_{24}:0.12\text{Eu}^{2+} \) phosphor (Figure 5), to generate high-quality white light.

The influence of the \( \text{Mn}^{2+} \) content on the luminescence spectra of \( \text{Ca}_{1.5}\text{Ba}_{7.38-y}\text{Lu}_2\text{Si}_6\text{O}_{24}:0.12\text{Eu}^{2+}/y\text{Mn}^{2+} \) phosphors (for \( y = 0, 0.1, 0.3, 0.5, 0.7, 0.9, \) and \( 1 \)), excited at 343 nm, is shown in Figure 6. These results suggest that codoping with \( \text{Eu}^{2+} \) and \( \text{Mn}^{2+} \) in the CBLSO host can generate tunable white light because blue-greenish and red light emission bands, centered at 484 and 500 nm (because of \( ^{4}S_{3/2} \) to \( ^{6}P_{1/2} \) transitions of \( \text{Eu}^{2+} \) ions), and also at 618 nm (because of \( ^{4}T_{1}(^{6}G) \) to \( ^{6}A_{1}(^{6}S) \) transitions of \( \text{Mn}^{2+} \) ions), were recorded.

The broad emission bands can be attributed to the transitions of \( \text{Eu}^{2+} \) and \( \text{Mn}^{2+} \) ions which occupy the three distinct \( \text{Ba} \) sites in the host. The PL intensity due to \( \text{Eu}^{2+} \) ions decreases, and the intensity of the red light emission owing to \( \text{Mn}^{2+} \) ions increases with the increase of the \( \text{Mn}^{2+} \) content (\( y \) value) up to \( y = 0.7 \). Further increase of the \( \text{Mn}^{2+} \) content resulted in a decrease in the intensity because of the concentration quenching effect.

Eu\(^{2+}\) and Mn\(^{2+}\) in the CBLSO host can generate tunable white light because blue-greenish and red light emission bands, centered at 484 and 500 nm (because of \( ^{4}F_{5/2} \) to \( ^{4}F_{7/2} \) transitions of \( \text{Eu}^{2+} \) ions), and also at 618 nm (because of \( ^{4}T_{1}(^{6}G) \) to \( ^{6}A_{1}(^{6}S) \) transitions of \( \text{Mn}^{2+} \) ions), were recorded.

The broad emission bands can be attributed to the transitions of \( \text{Eu}^{2+} \) and \( \text{Mn}^{2+} \) ions which occupy the three distinct \( \text{Ba} \) sites in the host. The PL intensity due to \( \text{Eu}^{2+} \) ions decreases, and the intensity of the red light emission owing to \( \text{Mn}^{2+} \) ions increases with the increase of the \( \text{Mn}^{2+} \) content (\( y \) value) up to \( y = 0.7 \). Further increase of the \( \text{Mn}^{2+} \) content resulted in a decrease in the intensity because of the concentration quenching effect.

The influence of the \( \text{Eu}^{2+} \) content in the codoped CBLSO:0.3Mn\(^{2+}\), \( z\text{Eu}^{2+} \) phosphors (i.e., the Mn\(^{2+}\) concentration was fixed at \( y = 0.3 \)) on the PL spectra is plotted in Figure 7 (for \( z = 0.04, 0.06, 0.08, 0.1, 0.12, \) and 0.15). The intensity of the red light emission of CBLSO phosphors due to Mn\(^{2+}\) remarkably enhances with the increase of the Eu\(^{2+}\) content up to \( z = 0.12 \). Further increase in the Eu\(^{2+}\) concentration (\( z = 0.12 \) and beyond) led to a decrease in the emission intensity, owing to the concentration quenching effect.

2.3.2. Energy Transfer. The above results (Figures 6 and 7) suggest that energy transfer from \( \text{Eu}^{2+} \) to \( \text{Mn}^{2+} \) ions should efficiently occur. The decay time is of great importance, as it can validate this hypothesis. Thus, the PL decay time profiles of \( \text{CBLSO}:0.12\text{Eu}^{2+}/y\text{Mn}^{2+} \) phosphors (for the same phosphors \( \text{Ca}_{1.5}\text{Ba}_{7.38-y}\text{Lu}_2\text{Si}_6\text{O}_{24}:0.12\text{Eu}^{2+}/y\text{Mn}^{2+} \), reported in 3.3.1 and Figure 6) were recorded by using an excitation wavelength at 343 nm and a monitored wavelength at 484 nm. The results, shown in the plots of Figure 8, were rendered well by the sum of two exponential decay components

\[
I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)
\]
where \( A_1 \) and \( A_2 \) are the exponential constants and \( \tau_1 \) and \( \tau_2 \) are the decay time constants. Thus, the average fluorescence decay times \( (\tau^*) \) can be calculated by the formula illustrated in eq 2.38

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

The results of the average fluorescence decay times \( (\tau^*) \), calculated by using eq 2, are presented in Figure 8. The fluorescence decay time decreases from 161 to 133, 105, 93, 70, 68, and 64 ns for \( y = 0, 0.1, 0.3, 0.5, 0.7, 0.9 \), and 1, respectively. The decrease in the decay time by increasing the \( \text{Mn}^{2+} \) concentration suggests that efficient energy transfer from \( \text{Eu}^{2+} \) to \( \text{Mn}^{2+} \) ions in CBLSO phosphors should occur.

The values of the energy-transfer efficiency, \( \eta \), from \( \text{Eu}^{2+} \) to \( \text{Mn}^{2+} \) ions were calculated for different \( \text{Mn}^{2+} \) concentrations using eq 3

\[
\eta = 1 - \frac{I_S}{I_{S0}}
\]

where \( I_S \) and \( I_{S0} \) are the values of luminescence intensity in the presence and absence of the activator \( \text{Mn}^{2+} \), respectively. The results, plotted in the diagram of Figure 9, suggest that the energy-transfer efficiency increases with the increase of the \( \text{Mn}^{2+} \) concentration. At the optimal concentration of \( \text{Mn}^{2+} (y = 0.7) \), the value of \( \eta \) is 67%.

The mechanism of the energy transfer from \( \text{Eu}^{2+} \) to \( \text{Mn}^{2+} \) can be investigated via Dexter's energy-transfer formula of multipolar interactions, and the following relation can be obtained

\[
\frac{I_{S0}}{I_S} \propto C^{n/3}
\]

where \( C \) represents the total concentration of the sensitizer \( \text{Eu}^{2+} \) and the activator \( \text{Mn}^{2+} \). The values of \( n \) are 6, 8, or 10 for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The plots of \( I_{S0}/I_S \) versus \( C^{n/3} \) are shown in Figure 10, for the three values of \( n: 6 \) (Figure 10a), 8 (Figure 10b), and 10 (Figure 10c). The best linear fitting is clearly seen for \( n = 6 \) (\( R^2 = 0.995 \), Figure 10a). This finding suggests that the energy transfer from the sensitizer \( \text{Eu}^{2+} \) to the activator \( \text{Mn}^{2+} \) in the CBLSO:Eu^{2+}/Mn^{2+} phosphors predominantly takes place through dipole–dipole interactions.

2.3.3. CIE Color Coordinates. The produced CBLSO phosphors present the ability to tune the color coordinates by just adjusting the concentrations of Ca and Mn. The plot of Figure 11 was created by excitation with UV light at 343 nm. Starting from point A (the precise contents in the phosphor are reported in the legend of the figure), the addition of \( \text{Mn}^{2+} \) (from \( y = 0 \) to 1) allows the tuning of the emitting color from blue-greenish (point A) to white and yellow (point B). Then, the increase of the Ca\(^{2+}\) content (from \( x = 0.6 \) to 0.9) can shift the emission light to the points C, D, and E, which are in the white area of the diagram.

These results qualify the produced CBLSO:Eu\(^{2+}/\text{Mn}^{2+}\) compositions as efficient color tunable phosphors, which can be considered as single-phase white light-emitting phosphors for application in WLEDs. The two photographs on the right-hand side of Figure 11 illustrate the prepared CBLSO:Eu\(^{2+}/\text{Mn}^{2+}\) phosphor powder under common daylight and its efficient white light under UV light excitation at 365 nm. The emission spectrum of the fabricated white LED lamp under 365 nm UV light is illustrated in Figure 12. High-quality white light was obtained, with CIE chromaticity coordinates (0.380, 330), which are positioned in the region of white light,
and can be efficiently tuned by varying the concentration of Ca\(^{2+}\), Eu\(^{2+}\), and Mn\(^{2+}\) cations. The inset of Figure 12 shows the white light-emitting lamp (LED lamp excited at 365 nm), which emits a warm white light by using a CBLSO:Eu\(^{2+}/\)Mn\(^{2+}\) phosphor in combination with a commercial 365 nm UV chip.

2.3.4. Influence of Temperature on PL Properties. The influence of the temperature on the PL of the produced phosphors was also investigated. The emission spectra recorded at different temperatures for the Ca-free (BLSO, \(x = 0\)) and the Ca-doped Ca\(_x\)Ba\(_{8.8-x}\)Eu\(_{0.2}\)Lu\(_2\)Si\(_6\)O\(_{24}\) phosphors for \(x = 0.15\) under excitation at 343 nm are plotted in Figure 13a,b, respectively. The intensity of the PL spectra decreases with the increase of temperature. This can be associated with the fact of the increased probability of nonradiative transition induced by thermal activation and the release of the luminescent center through the crossing point between the excited state and the ground state. The color of the emission remains unchanged with the rise of temperature. This suggests that these phosphors have a stable color quality even at high temperatures. However, a decrease in the intensity with the increase of temperature was recorded.

The differences in the decrease of emission intensity for the Ca-free (BLSO:Eu\(^{2+}\)), the single Ca-doped (CBLSO:0.12Eu\(^{2+}\)), and the codoped phosphors (CBLSO:Eu\(^{2+}/\)Mn\(^{2+}\)) at temperatures between room temperature (RT) and 150 °C are shown in the curves in Figure 13c. It is clearly seen that doping of the BLSO host favors the temperature stability of PL. The best behavior was recorded with the codoped phosphors. The improvement in the thermal stability might be related to two phenomena. The first one deals with the contraction of the unit cell volume, which occurs because of the substitution of the smaller Ca\(^{2+}\) cations for the larger Ba\(^{2+}\) cations in the BLSO phosphor host. This should increase the structural rigidity of the host and affect the interactions between Eu\(^{2+}\) and O\(^{2-}\) ions (related to nephelauxetic and crystal field effects of the 5d orbital of Eu\(^{2+}\)) which vary.\(^{40,41}\) On the other hand, the increase in the content of Ca\(^{2+}\) ions favors the movement of the activator Eu\(^{2+}\) ions from the Ba(1) sites to the Ba(2) and Ba(3) sites. Because the Ba(2) and Ba(3) sites are smaller than the Ba(1) sites, the former should have smaller bond length with...
3. CONCLUSIONS

Single-phase full color-emitting Eu\(^{3+}/\)Mn\(^{2+}\) codoped CBLSO phosphors were successfully synthesized using a high-temperature solid-state reaction method. The produced phosphors can perfectly match the needs of a UV LED chip because they exhibit a broad excitation band, which ranges from 200 to 450 nm with the maximum peak at 343 nm. The substitution of larger Ba\(^{2+}\) ions by smaller Ca\(^{2+}\) ions distributes the Eu\(^{2+}\) activator ions among the available sites Ba(1), Ba(2), and Ba(3) in the CBLSO host, which broadens the emission spectra and improves thermal stability. The luminescence of the produced CBLSO phosphors can be further improved by the substitution of Mn\(^{3+}\) ions at a specific amount. The luminescence spectra, the calculated energy-transfer efficiency, and the decay times of the produced phosphors suggested that an efficient energy transfer from Eu\(^{2+}\) to Mn\(^{2+}\) ions occurs in the CBLSO host, which takes place predominantly through dipole–dipole interactions. The emission of the produced CBLSO phosphors can be efficiently tuned by merely adjusting the amounts of the doping ions, and high-quality tunable white light emission can be achieved.

4. MATERIALS AND EXPERIMENTAL PROCEDURE

A series of BLSO-based phosphors were synthesized by a high-temperature solid-state reaction route (the precise compositions are presented in the section of the Results and Discussion). Fine powders of CaCO\(_3\), BaCO\(_3\), SiO\(_2\), MnCO\(_3\) (99.99% purity Sinopharm Chemical Reagent Co. Ltd., Shanghai, PR China), Lu\(_2\)O\(_3\), and Eu\(_2\)O\(_3\) (99.99%, Yuelong Co. Ltd, Shanghai, PR China) were used as raw materials. Powder mixtures of the raw materials in stoichiometric proportions were thoroughly mixed and ground in an Si\(_3\)N\(_4\) mortar. The homogeneous mixtures were transferred to alumina crucibles, which were then put into a horizontal tubular furnace and heated at 1400 °C for 4 h under flowing NH\(_3\) gas (the heating rate was 300 K/h). Then, the synthesized samples were cooled naturally to RT inside the furnace under flowing NH\(_3\) gas. Fine powders were obtained (by grinding) for further characterization.

The crystallized phases of the synthesized samples were identified by X-ray diffraction analysis (Philips PW 1700, using Cu K\(_{\alpha1}\) radiation, \(\lambda = 1.54056\) Å, at 40 kV, and 100 mA, with a graphite monochromator). The samples were placed in a silica chip, which was positioned vertically in the equipment with a 20/0 scan axis. The data were recorded in the range between 20° and 60°, with a scanning rate of 0.5°/min and a step of 20/0.0167°.

The PLE and emission spectra were measured by using a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The spectra of PL of both the excitation and emission were corrected for the spectral response of a monochromatic and Hamamatsu R928P photomultiplier tube (Hamamatsu Photonics K.K., Hamamatsu, Japan) by a light diffuser and tungsten lamp (NOMA Electric Corp, NY; 10 V, 4 A).

The thermal stability of the phosphor at selected compositions was evaluated by recording the PL spectra at different temperatures. More specifically, the phosphor was placed on an aluminum plaque with cartridge heaters. The temperature was measured by thermocouples put inside the plaque and controlled with a standard TAP-02 high-temperature fluorescence controller. Starting from RT, the PL spectrum was recorded. Then, the temperature was increased, and when it was stabilized, the PL spectrum was recorded. Next, the temperature was fixed at a higher value, and the PL spectrum was recorded at that temperature. Measurements were conducted at RT, 50, 75, 100, 125, and 150 °C.

### References

1. Schlotter, P.; Schmidt, R.; Schneider, J. Luminescence conversion of blue light emitting diodes. *Appl. Phys. A: Mater. Sci. Process.* 1997, 64, 417–418.
2. Shi, Y.; Zhu, G.; Mikami, M.; Shimomura, Y.; Wang, Y. A novel Ce\(^{3+}\) activated Lu\(_2\)MgAl\(_3\)Si\(_2\)O\(_8\) garnet phosphor for blue chip light-emitting diodes with excellent performance. *Dalton Trans.* 2015, 44, 1775–1781.
3. Wu, H.; Zhang, X.; Guo, C.; Xu, J.; Wu, M.; Su, Q. Three-band white light from InGaN-based blue LED chip precoated with green/red phosphors. *IEEE Photonics Technol. Lett.* 2005, 17, 1160–1162.
4. Xia, Z.; Xu, Z.; Chen, M.; Liu, Q. Recent developments in the new inorganic solid-state LED phosphors. *Dalton Trans.* 2016, 45, 11214–11232.
5. Yang, W.-J.; Luo, L.; Chen, T.-M.; Wang, N.-S. Luminescence and energy transfer of Eu- and Mn-coactivated CaAl\(_2\)Si\(_2\)O\(_8\) as a potential phosphor for white-light UVLED. *Chem. Mater.* 2005, 17, 3883–3888.
6. Chen, Y.; Gong, M.; Wang, G.; Su, Q. High efficient and low color-temperature white light-emitting diodes with Tb\(_3\)Al\(_5\)O\(_12\):Ce\(^{3+}\) phosphor. *Appl. Phys. Lett.* 2007, 91, 071117.
7. Kate, O. M.; Zhang, Z.; Dorenbos, P.; Hintzen, H. T.; van der Kolk, E. 4f and 5d energy levels of the divalent and trivalent lanthanide ions in M\(_2\)Si\(_3\)N\(_6\) (M=Ca, Sr, Ba). *J. Solid State Chem.* 2013, 197, 209–217.
8. Jung, Y. W.; Lee, B.; Singh, S. P.; Sohn, K.-S. Particle-swarm-optimization-assisted rate equation modeling of the two-peak emission behavior of non-stoichiometric CaAl\(_2\)Si\(_2\)O\(_8\):Eu\(^{2+}\) phosphors. *Opt. Express* 2010, 18, 17805–17818.
9. Hu, W.-W.; Ji, W.-W.; Khan, A. A.; Hao, L.-Y.; Xu, X.; Yin, L.-J.; Agathopoulos, S. Preparation of Sr\(_{1-x}\)Ca\(_{x}\)Li\(_{1-x}\)Al\(_{x}\)N\(_{2}\):Eu\(^{2+}\) solid solutions and their photoluminescence properties. *J. Am. Ceram. Soc.* 2016, 99, 3273–3279.
10. Huang, C.-H.; Chen, T.-M. Novel yellow-emitting Sr\(_3\)Mg\(_2\)O\(_{10}\)(PO\(_4\))\(_2\):Eu\(^{3+}\) (Ln = Y, La) phosphors for applications in white LEDs with excellent color rendering index. *J. Inorg. Chem.* 2011, 50, 5725–5730.
11. Xia, Z.; Liu, Q. Progress in discovery and structural design of color conversion phosphors for LEDs. *Prog. Mater. Sci.* 2016, 84, 59–117.
12. Khan, S. A.; Hao, Z.; Hu, W.-W.; Hao, L.-Y.; Xu, X.; Khan, N. Z.; Agathopoulos, S. Novel single-phase full-color emitting...
BaLu2Si6O24:Ce3+/Mn2+/Tb3+ phosphors for white LED applications. J. Mater. Sci. 2017, 52, 10927—10937.

(11) Li, G.; Li, C.; Zhang, C.; Cheng, Z.; Quan, Z.; Peng, C.; Lin, J. Tm3+ and/or Dy3+ doped LaOCl nanocrystalline phosphors for field emission displays. J. Mater. Chem. 2009, 19, 8936—8943.

(12) Li, G.; Geng, D.; Shang, M.; Zhang, Y.; Peng, C.; Cheng, Z.; Lin, J. Color tuning luminescence of Ce3+/Mn2+/Tb3+—Tricatologated Mg2+(PO4)2 via energy transfer: potential single-phase white-light-emitting phosphors. J. Phys. Chem. C 2011, 115, 21882—21892.

(13) Huang, C.-H.; Chiu, Y.-C.; Yeh, Y.-T.; Chan, T.-S.; Chen, T.-M. Eu2+-activated Sr2ZnSc2PO7: a novel near-ultraviolet converting yellow-emitting phosphor for white-light emitting diodes. ACS Appl. Mater. Interfaces 2012, 4, 6661—6668.

(14) Xia, Z.; Zhang, Y.; Molokeev, M. S.; Atuchin, V. V.; Luo, Y. Linear structural evolution induced tunable photoluminescence in chrynomyyxine solid-solution phosphors. Sci. Rep. 2013, 3, 3310.

(15) Gauthier, R.; Li, X.; Xia, Z.; Massuyeau, F. Two-step design of a single-doped white phosphor with high color rendering. J. Am. Chem. Soc. 2017, 139, 1436—1439.

(16) Chen, M.; Xia, Z.; Molokeev, M. S.; Wang, Y.; Liu, Q. Tuning of photoluminescence and local structures of substituted cations in xSr2Ca(PO4)2:Eu2+ (0 ≤ x ≤ 2) solid solution phosphors. Chem. Mater. 2017, 29, 1430—1438.

(17) Khan, S. A.; Ji, W.; Hao, L.; Xu, X.; Agaphtopolous, S.; Khan, N. Z. Synthesis and characterization of Ce3+/Tb3+ co-doped CaLa4Si3O12 phosphors for application in white LED. Opt. Mater. 2017, 72, 637—643.

(18) Tang, J.; Chen, J.; Hao, L.; Xu, X.; Xie, W.; Li, Q. Green Eu2+-doped BaSr2Si2O7:N3+ phosphor for white-light emitting diodes: synthesis, characterization and theoretical simulation. J. Lumin. 2011, 131, 1101—1106.

(19) Sato, Y.; Kato, H.; Kobayashi, M.; Masaki, T.; Yoon, D.-H.; Kakihana, M. Tailoring of deep-red luminescence in Ca3SiO4:Eu2+. Angew. Chem., Int. Ed. 2014, 53, 7756—7759.

(20) Park, J. K.; Kim, J. M.; Oh, E. S.; Kim, C. H. Luminescence properties of Eu2+–activated CaAlSiO4 by photoluminescence spectra. Electrochem. Solid-State Lett. 2005, 8, H6—H8.

(21) Zhang, X.; Wang, J.; Huang, L.; Pan, F.; Chen, Y.; Lei, B.; Peng, M.; Wu, M. Tunable luminescent properties and concentration-dependent, site-preferable distribution of Eu2+ ions in silicate glass for white LEDs applications. ACS Appl. Mater. Interfaces 2015, 7, 10044—10054.

(22) Lu, L.-C.; Cai, C.; Zhu, Q.-Q.; Tang, J.-Y.; Hao, L.-Y.; Xu, X. Color tunable Sr3SiO4:Eu2+ phosphors through the modification of crystal structure. J. Mater. Sci.: Mater. Electron. 2013, 24, 4516—4521.

(23) Xia, Z.; Liu, H.; Li, X.; Liu, C. Identification of the crystallographic sites of Eu2+ in Ca3NaMg2(PO4)2: structure and luminescence properties study. Dalton Trans. 2013, 42, 16588—16595.

(24) Han, J.; Zhou, W.; Qiu, Z.; Yu, L.; Zhang, J.; Xie, Q.; Wang, J.; Lian, S. Redistribution of activator photoluminescence by isovalent and alivalent cation substitutions in whitlockite phosphors. J. Phys. Chem. C 2015, 119, 16585—16595.

(25) Li, G.; Lin, C. C.; Chen, W.-T.; Molokeev, M. S.; Atuchin, V. V.; Chiang, C.-Y.; Zhou, W.; Wang, C.-W.; Li, W.-H.; Sheu, H.-S.; Chan, T.-S.; Ma, C.; Liu, R.-S. Photoluminescence tuning via cation substitution in oxonitridosilicate phosphors: DFT calculations, different site occupations, and luminescence mechanisms. Chem. Mater. 2014, 26, 2991—3001.

(26) Ji, H.; Huang, Z.; Xia, Z.; Molokeev, M. S.; Atuchin, V. V.; Huang, S. Cation substitution dependent bimodal photoluminescence in whitlockite structural Ca2−xSr2x(PO4)2:Eu2+ (0 ≤ x ≤ 2) solid solution phosphors. Inorg. Chem. 2014, 53, 11119—11124.

(27) Ju, L.-C.; Xu, X.; Hao, L.-Y.; Liu, Y.; Lee, M.-H. Modification of the coordination environment of Eu2+ in Sr2SiO4:Eu2+ phosphors to achieve full color emission. J. Mater. Chem. C 2015, 3, 1567—1575.

(28) Liu, Y.; Zhang, C.; Cheng, Z.; Zhou, Z.; Jiang, J.; Jiang, H. Origin and luminescence of anomalous red-emitting center in rhombohedral Ba2Lu2Si6O24:Eu2+ blue phosphor. Inorg. Chem. 2016, 55, 8628—8635.