Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$：Dy$^{3+}$荧光粉的制备及其荧光性能

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Abstract: The single phase full color phosphors of Dy$^{3+}$-doped Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$ were synthesized by a solid-state reaction method. The as-synthesized phosphors were characterized by X-ray diffraction and photoluminescence spectroscopy. These phosphors can be efficiently excited in a near ultraviolet limit of 350 nm. The influences of sintering temperature, concentration and charge compensators (Li$^+$, Na$^+$ or K$^+$) on the emission intensity were investigated. The results show that the most intensive emission intensity of the Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$:Dy$^{3+}$ phosphor, which is prepared with Na$^+$ ions at the sintering temperature of 950 ℃ and the Dy$^{3+}$ doping concentration of 4.0 mol%, can be obtained. It is indicated that Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$:Dy$^{3+}$ can be used as a promising luminescent material for near ultraviolet(NUV)-based white-emitting diodes.

Key words: phosphors; dysprosium-dope chlorosilicate; luminescence; charge compensations; white light-emitting diodes

1 Introduction

Recent studies focus on white light-emitting diodes (white-LEDs) due to their advantages such as low energy consumption, high reliability, long lifetime, fast response and non-polluting. [1–3] The existing two methods are used to generate white light. One method is the use of blue LED with yellow emitting phosphor and the another is the application of red/green/blue tricolor phosphors excited by near-ultraviolet (NUV) LED chips. [4–6] However, there exist some problems needed to be solved, such as color changes...
with input power, low color rendering index due to two-color mixing and low color reproducibility as well. In order to solve these problems, much effort has been paid and single-phase white light emitting phosphors based on UV/NUV chips have been investigated.[7–9] The white light emission resulted from a single matrix phosphor can obtain a high luminous efficacy because it can avoid multi-phosphors re-absorption of emission colors. Therefore, it is necessary for the improvement of the luminescence reproducibility and efficiency to develop single matrix phosphors with a good stability.[10–13]

As known, Dy$^{3+}$ ion is one of the important rare earth ions for the preparation of phosphors and plays a major role in the production of white light luminescent materials. Dy$^{3+}$ doped phosphors exhibit several excitation peaks in UV and blue range, and Dy$^{3+}$ doped materials usually have three visible emission bands, i.e., the blue emission at about 486 nm, the yellow emission at about 575nm and the feeble red emission at about 665 nm, corresponding to the transitions of $^4F_{9/2} \rightarrow ^6H_{15/2}, ^4F_{9/2} \rightarrow ^6H_{11/2}$ and $^4F_{9/2} \rightarrow ^6H_{11/2}$, respectively.[14] The yellow emission of Dy$^{3+}$ ion is particularly hypersensitive to local environment, while its blue emission is slightly influenced by the outside surroundings.[15] Since the luminescence properties of Dy$^{3+}$ depend on local environment in a given host material, it is possible to achieve near white light emission by adjusting the yellow to blue intensity ratio value.[16–18] Therefore, Dy$^{3+}$ doped materials have been intensively investigated in recent years, such as borates (Sr$^3$(BO$_3$)$_2$:Dy$^{3+}$),[5] silicates (Li$_2$SrSiO$_4$:Dy$^{3+}$),[13] aluminates (Sr$_2$MgAl$_2$O$_6$:Dy$^{3+}$),[16] molybdates (SrMoO$_4$:Dy$^{3+}$),[17] titanates (YNbTiO$_6$:Dy$^{3+}$)[18] and alkaline earth chloride silicate (Ca$_8$Mg(Sr$_1$)$_4$(Cl$_2$:Dy$^{3+}$).[19] Among these phosphors, alkaline earth chloride silicate is attracted much attention due to the low synthesis temperature and high chemical stability.

Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$ as a matrix material for Eu$^{2+}$ doped phosphor emitting luminescence has been investigated.[20–22] However, the luminescence properties of Dy$^{3+}$-doped Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$ phosphors are still unclear yet. In this paper, Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$:Dy$^{3+}$ phosphors were synthesized by a conventional solid-state reaction method. The effects of sintering temperature, Dy$^{3+}$-doped concentration and charge compensation of Li$^+$, Na$^+$ and K$^+$ ions on the emission intensity were investigated. In addition, the CIE chromaticity coordinates of the phosphor were also calculated.

2 Experimental

The phosphor samples of Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$:Dy$^{3+}$ were prepared by a conventional solid-state reaction method. The starting materials used are analytical pure CaO, SiO$_2$, CaCl$_2$, SrCO$_3$ and the rare earth dopant Dy$_2$O$_3$ (99.99%). In some cases, an appropriate amount of analytical pure Li$_2$CO$_3$, Na$_2$CO$_3$ or K$_2$CO$_3$ was added as a charge compensator. The required stoichiometrical amounts of raw materials were thoroughly mixed with the excessive amount of CaCl$_2$ (50% in mole) as a flux and ground in an agate mortar. The well-mixed reactants were placed in an alumina crucible closed with a lid and preheated in a muffle furnace in air at 500 °C for 2 h. Then, the preheated mixtures were ground sufficiently again after cooling and subsequently fired at 850–1000 °C for 3 h. The sintered cake was ground and washed with hot de-ionized water to remove the excess CaCl$_2$. The required phosphor samples were obtained after drying.

The X-ray powder diffraction (XRD) patterns of the samples were determined on a model Rigaku-miniflex II X-ray diffractometer with Cu K$_\alpha$ radiation (λ = 0.154 06 nm) at 35 kV and 25 mA. The emission and excitation spectra were measured on a model FL/FS920 fluorescence luminous spectrometer with a 450 W Xe lamp as an excitation source. All the measurements were performed at room temperature.

3 Results and discussion
3.1 XRD analysis

Fig. 1 shows the XRD patterns of the Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$:0.01Dy$^{3+}$ phosphors sintered at different temperatures for 3 h. It is seen that the phase of Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$ does not appear at the sintering temperature of 850 °C. The main phase of Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$ appears when the sintering temperature increases to 900 °C, which is confirmed by the standard powder diffraction file (JCPDS 43–0085). The crystallinity of Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$ can be improved when the temperature is further increased, and the pure phase appears completely at 950 °C. The results indicate that the positions and relative intensities of the diffraction peaks of the as-prepared samples are consistent with JCPDS 43–0085, and the doping Dy$^{3+}$ ion at a small content does not change the crystal structure of the matrix. According to JCPDS card No. 43–0085, Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$ belongs to the monoclinic crystal system. The unit cell volume and lattice parameters of the matrix are 4.619 3 nm$^3$, $a = 1.870$ 3 nm, $b = 1.434$ 4 nm, $c = 1.848$ 1 nm, $\beta = 111.30^\circ$ and $Z = 8$.

![Fig. 1 XRD patterns of Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$:0.01Dy$^{3+}$ phosphors sintered at different temperatures for 3 h](image)

3.2 Effect of sintering temperatures on luminescent properties

Sintering temperature is a critical factor affecting the crystalline and luminescent properties of phosphors. Fig. 2 shows the emission ($\lambda_{ex}=350$ nm) spectra of Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$:0.01Dy$^{3+}$ prepared at various sintering temperatures for 3 h. Clearly, the position and shape of emission peaks are not changed with sintering temperature. The emission intensities increase with increasing the sintering temperature from 900 °C to 950 °C for the improvement of the crystallinity of phosphors. The maximum luminescence intensity of the phosphors can be obtained at the sintering temperature of 950 °C. However, the emission intensity of the phosphors decreases significantly when the sintering temperature is up to 1000 °C. This may be due to the aggregation and clump of samples. It is indicated that the Ca$_6$Sr$_4$(Si$_2$O$_7$)$_3$Cl$_2$:Dy$^{3+}$ phosphors with an intensive emission intensity can be prepared at the optimum sintering temperature of 950 °C.
3.3 Luminescence properties of the Ca₆Sr₄(Si₂O₇)₃Cl₂:0.01Dy³⁺ phosphors

Fig. 3 shows the excitation (monitored at 575 nm) and emission (excited by 350 nm) spectra of the Ca₆Sr₄(Si₂O₇)₃Cl₂:0.01Dy³⁺ phosphors. All the profiles of excitation and emission spectra at different concentrations of Dy³⁺ ions are similar. For instance, the excitation spectrum of Ca₆Sr₄(Si₂O₇)₃Cl₂:0.01Dy³⁺ phosphor has several intensive excitation bands centered at 325, 350, 365, 387, 425, 450 and 473 nm, which are corresponding to the transitions of Dy³⁺ from the $^6H_{15/2}$ ground state to $^6P_{3/2}, ^6P_{7/2}, ^4D_{5/2}, ^4M_{21/2}, ^4G_{11/2}, ^4J_{15/2}$ and $^4F_{9/2}$, respectively [12]. Clearly, the Ca₆Sr₄(Si₂O₇)₃Cl₂:Dy³⁺ phosphors can be effectively excited by NUV and blue radiation. As some peaks located at UV region are more intense than that of blue region, the Ca₆Sr₄(Si₂O₇)₃Cl₂:Dy³⁺ phosphor is more suitable for UV LED chip than blue LED chip. Besides, the band centered at 350 nm possesses the maximum intensity among these excitation bands. Thereby, the emission spectra are monitored at 350 nm in order to investigate the emission intensity of the phosphors.

In Fig. 3(b), the emission spectrum of Ca₆Sr₄(Si₂O₇)₃Cl₂:0.01Dy³⁺ phosphor exhibits three emission bands centered at 486 (blue), 575 (yellow) and 665 nm (red) under 350 nm excitation, which are attributed to the transitions of $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^4F_{9/2} \rightarrow ^6H_{13/2}$ and $^4F_{9/2} \rightarrow ^6H_{11/2}$ of Dy³⁺, respectively [14]. The blue emission band is composed of two peaks centered at 482 and 493 nm in the range of 460–510 nm, which may be due to the energy level splitting of the Ca₆Sr₄(Si₂O₇)₃Cl₂ crystal field [18]. Also, the yellow emission at 575 nm is more intense than the blue emission at 486 nm. It is well known that $^4F_{9/2} \rightarrow ^6H_{13/2}$
transition of Dy\(^{3+}\) belongs to hypersensitive transitions with (\(\Delta L = 2, \Delta J = 2\)). When Dy\(^{3+}\) is located at a low-symmetry local site (without an inversion center), this emission transition dominates in emission spectra, otherwise, the blue emission is dominant.\(^{[15]}\) It is thus assumed that Dy\(^{3+}\) could be located at a low symmetry in Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):Dy\(^{3+}\) phosphors.

3. 4 Effect of concentration of Dy\(^{3+}\) on luminescence properties

The doping concentration is one of the important factors influencing the performance of luminescent materials. Figs. 4 and 5 show the emission spectra of Dy\(^{3+}\)-doped Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\) phosphors with different Dy\(^{3+}\) concentrations excited at 350 nm. The shapes and position of emission peaks of Dy\(^{3+}\)-doped Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\) phosphors are independent of doping concentration, but the emission intensity changes with the Dy\(^{3+}\) concentration. The emission intensity initially enhances with increasing Dy\(^{3+}\) concentration. The intensity achieves a maximum value when \(x = 0.04\) and decreases when \(x < 0.04\) due to the self-concentration quenching effect, reflecting that the optimal doping concentration of Dy\(^{3+}\) is 4.0% in mole.

![Emission spectra of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):Dy\(^{3+}\) phosphors with different concentrations of Dy\(^{3+}\) (\(x = 0.005-0.060\)).](image)

Fig. 4 Emission (\(\lambda_{\text{ex}}=350\) nm) spectra of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):xDy\(^{3+}\) phosphors with different concentrations of Dy\(^{3+}\) (\(x = 0.005-0.060\)).

![Intensities of different emission peaks of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):xDy\(^{3+}\) phosphors.](image)

Fig. 5 Intensities of different emission peaks of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):xDy\(^{3+}\) phosphors.

3. 5 Mechanism of the energy transfer between Dy\(^{3+}\) ions

As known, the self-concentration quenching is mostly due to the interaction of the electric multipoles during the resonance transfer. Multipolar interactions are usually prevalent, which have several types, such as dipole–dipole (\(d–d\)), dipole–quadrupole (\(d–q\)), and quadrupole–quadrupole (\(q–q\)) interactions. According to the Dexter theory,\(^{[23]}\) the relation between luminescent intensity(\(I\)) and the activator doping amount (\(x\))
can be expressed by \[ \lg \left( \frac{I}{x} \right) = A - \frac{\theta}{3} \lg x \] 

where \( A \) is a constant for one host, when the value of \( \theta \) is 6, 8 and 10, the interaction type is dipole–dipole (\( d-d \)), dipole–quadrupole (\( d-q \)) and quadrupole–quadrupole (\( q-q \)), respectively. Based on the result of calculation, the value of \( \theta \) is approximately equal to 5.70, which is close to 6. Fig. 6 shows the \( \lg(I/x) - \lg(x) \) plot for the \( ^{4}F_{9/2} \to ^{6}H_{15/2} \) transition of Dy\(^{3+}\) in Ca\(_{6}\)Sr\(_{4}\)(Si\(_{2}\)O\(_{7}\))\(_{3}\)Cl\(_{2}\):xDy\(^{3+}\) phosphors (\( \lambda_{ex}=350 \) nm). It is seen that the dependence of \( \lg(I/x) \) on \( \lg x \) is linear and the slope is -1.9. According to Eq. (1), the corresponding value of \( \theta \) is 5.8. The experimental data are matched well with the calculated results. It is indicated that the energy transfer mechanism among the Dy\(^{3+}\) luminescence centers in Ca\(_{6}\)Sr\(_{4}\)(Si\(_{2}\)O\(_{7}\))\(_{3}\)Cl\(_{2}\):xDy\(^{3+}\) phosphors should be predominantly attributed to dipole-dipole interaction.

\begin{align*}
\text{Fig. 6} & \text{ The dependence of } \lg(I/x) \text{ on } \lg x \text{ in Ca}_{6}\text{Sr}_{4}(\text{Si}_{2}\text{O}_{7})_{3}\text{Cl}_{2}:xDy^{3+} \text{ phosphors (} \lambda_{ex}=350 \text{ nm).} \\
\text{The critical distance (} R_c \text{) is roughly calculated to reveal the average distance between the nearest Dy}^{3+} \text{ in the phosphors. The } R_c \text{ of the energy transfer between the same activators Dy}^{3+} \text{ in the phosphors can be estimated by} [25] \] 

\[ R_c = 2 \left[ \frac{3V}{4\pi X_c N} \right]^{1/3} \] 

where \( V \) is the volume of the unite cell, \( X_c \) is the critical concentration of the activator ion, and \( N \) is the number of the Ca\(^{2+}\) in the unit cell. By taking the experimental and analytic values of \( V, N \) and \( X_c \) (i.e., 4.619 3 nm\(^3\), 48, 0.04, respectively), we obtain that the critical transfer distance is 1.662 5 nm.

3.6 Effect of charge compensator on the emission intensity

The charge compensator plays an important role in improving the luminescence efficiency of phosphors. In order to investigate the effect of charge compensators, Li\(^{+}\), Na\(^{+}\) and K\(^{+}\) ions on the emission of Ca\(_{6}\)Sr\(_{4}\)(Si\(_{2}\)O\(_{7}\))\(_{3}\)Cl\(_{2}\):xDy\(^{3+}\), Li\(_2\)CO\(_3\), Na\(_2\)CO\(_3\) or K\(_2\)CO\(_3\) of 4.0% in mole were added as a charge compensator, respectively. It is regarded that the Dy\(^{3+}\) ions will replace partially Ca\(^{2+}\) ions and become the luminescent center of Ca\(_{6}\)Sr\(_{4}\)(Si\(_{2}\)O\(_{7}\))\(_{3}\)Cl\(_{2}\):xDy\(^{3+}\) phosphors. The radius of Dy\(^{3+}\) ions (i.e., 0.091 nm) is similar to the radius of Ca\(^{2+}\) ions (i.e., 0.100 nm), compared to the radius of Sr\(^{2+}\) ions (i.e., 0.118 nm). The electropositive defect luminescent center Dy\(_{Ca}^{3-}\) will be formed due to the unbalanced charge between Dy\(^{3+}\) ions and Ca\(^{2+}\) ions. To compensate the electropositive of Dy\(_{Ca}^{3-}\), alkali ions are added as charge compensators, and the effect of alkali ions on the emission intensity was investigated. The mechanism of charge compensations may be that two Ca\(^{2+}\) ions are replaced by one Dy\(^{3+}\) ion and one monovalence alkali
ion (Li\(^{+}\), Na\(^{+}\) or K\(^{+}\)), which can be expressed by

\[
2\text{Ca}^{2+} \rightarrow \text{Dy}^{3+} + \text{Na}^{+} (\text{Li}^{+} \text{or K}^{+})
\]  

(3)

Figure 7 shows the emission spectra of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):Dy\(^{3+}\) with different charge compensator ions. It is seen that the emission intensity of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):Dy\(^{3+}\),Na\(^{+}\) is more intense than that of the others. The emission intensity of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):Dy\(^{3+}\),Na\(^{+}\) is 1.75 times greater than that of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):Dy\(^{3+}\). This is attributed to that the radius of Na\(^{+}\) ion (i.e., 0.102 nm) is similar to that of Ca\(^{2+}\) ion (i.e., 0.100 nm), while the other charge compensators will induce more crystal lattice distortion due to the difference between the radius of Ca\(^{2+}\) ion and the radius Li\(^{+}\) ion (i.e., 0.076 nm) or the radius of K\(^{+}\) ion (i.e., 0.138 nm). The results indicate that Na\(^{+}\) ion is an appropriate charge compensator for Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):Dy\(^{3+}\) phosphors.

![Emission spectra](image)

Fig. 7 Influence of charge compensator ions (Li\(^{+}\), Na\(^{+}\) and K\(^{+}\)) on emission spectra of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):0.04Dy\(^{3+}\).

### 3.7 The CIE chromaticity coordinates of samples

Color coordinate is an important parameter for phosphors in white LED application. The CIE chromaticity coordinates and yellow light (Y) (\(\lambda = 575\) nm) / blue light (B) (\(\lambda = 482\) nm) ratios of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):xDy\(^{3+}\) phosphors with different Dy\(^{3+}\) concentrations were calculated from the emission (\(\lambda_{ex} = 350\) nm) spectra (see Fig. 3) by using the CIE 1931 color matching functions (see Table 1). The chromaticity coordinates of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):xDy\(^{3+}\) phosphors are nearly located as (\(x = 0.35, y = 0.42\)), which are in the edge of white light region. The Y/B ratio increases slightly with the increase of Dy\(^{3+}\) concentration, and the coordinate \(x\) changes slightly but the coordinate \(y\) does not vary. It is believed that the color coordinates of Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):Dy\(^{3+}\) phosphors should be also modulated by co-doping some other rare earth elements to change the Y/B ratio. Thus, Ca\(_6\)Sr\(_4\)(Si\(_2\)O\(_7\))\(_3\)Cl\(_2\):Dy\(^{3+}\) could be a promising single phase full color phosphor for white-LEDs.

<table>
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<th>(x) (content of Dy(^{3+}))/mol</th>
<th>CIE chromaticity coordinates</th>
<th>Y/B ratio</th>
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<tr>
<td>0.05</td>
<td>(0.36, 0.42)</td>
<td>1.31</td>
</tr>
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</table>
4 Conclusions

The Ca₆Sr₄(Si₂O₇)₃Cl₂:Dy³⁺ white-LED phosphors were prepared by a solid-state reaction technique. The crystallinity and phase purity of the Ca₆Sr₄(Si₂O₇)₃Cl₂ powders were characterized by X-ray diffraction. The excitation spectra illustrated that the phosphor could be effectively excited by NUV LED emission wavelength (350 nm). The optimum doping concentration of Ca₆Sr₄(Si₂O₇)₃Cl₂:Dy³⁺ phosphors was 4.0% in mole. It was indicated that the concentration quenching mechanism of ⁴F₉/₂ → ⁶H₁₃/₂ transition of Dy³⁺ ions in Ca₆Sr₄(Si₂O₇)₃Cl₂ phosphors is the dipole–dipole interaction. The Na⁺ ions could effectively improve the luminescent intensity due to its charge complementary function. The chromaticity coordinates of Ca₆Sr₄(Si₂O₇)₃Cl₂:Dy³⁺ phosphors were located in the near-white region. Ca₆Sr₄(Si₂O₇)₃Cl₂:Dy³⁺ phosphors could be used as a promising single phase full color phosphor for NUV-based white-LEDs.

References:


