Synthesis, photoluminescence properties and energy transfer studies of color-adjustable CaSrSiO₄:Ce³⁺,Li⁺,Mn²⁺ phosphors

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Abstract

A series of color tunable phosphors CaSrSiO₄:Ce³⁺,Li⁺,Mn²⁺ were synthesized by the traditional high temperature solid-state method. The as-prepared CaSrSiO₄:Ce³⁺,Li⁺,Mn²⁺ phosphors exhibit a broad excitation band ranging from 250 to 400 nm and give a blue emission band centered at 450 nm. When Mn²⁺ ions are codoped for the fabrication of CaSrSiO₄:Ce³⁺,Li⁺,Mn²⁺ phosphors, another new red-emitting peak appears at near 650 nm corresponding to the spin-forbidden 4T₁(6G)→4A₁(6S) transition of the Mn²⁺ ions. By adjusting the relative concentration of the Ce³⁺ and Mn²⁺ ions, the CIE chromaticity coordinate can be modulated from (0.156, 0.106) to (0.224, 0.211) owing to the energy transfer from Ce³⁺ to Mn²⁺ ions. The dipole–quadrupole interaction predominates in the energy transfer mechanism. The temperature dependent photoluminescence properties prove that the CaSrSiO₄ host has a good thermal stability. These results indicate that CaSrSiO₄:Ce³⁺,Li⁺,Mn²⁺ samples show tunable blue/red dual-wavelength emission depending on the codoped ions, which might have potential applications in the white light emitting diodes (wLEDs) and functional sunlight spectrum conversion device as greenhouse for green agriculture.

1. Introduction

In recent years, inorganic phosphor materials have demonstrated important application for the wavelength-conversion in some fields [1–5]. For example, phosphor materials can be firstly used in the white light emitting diodes (wLEDs) and they can convert the near-UV light or blue light into the other visible light, such as blue, green, yellow or red light; thus white light can be produced in such a way for general lighting or illumination [1,2]. Secondly, phosphor materials can also be used for the improvement of the efficiency of the solar cell via the down-conversion or up-conversion process to realize the near infrared emission [3]. Moreover, phosphors can also be used to fabricate the functional sunlight spectrum conversion device as greenhouse for green agriculture via the blue/red dual-wavelength emission [4]. As for such applications, we often hope that light can be absorbed and emitted with high efficiency and broad spectral section. As far as we know, many matrices doped with rare earth ions such as Eu²⁺ and Ce³⁺ have excellent luminescent properties with broad-band excitation and emission. Among them, silicate based phosphors especially the orthosilicates based phosphors have drawn much attention in the phosphor research areas. Due to the abundant phase transformation and rigid crystal structure of orthosilicates, some groups have reported lots of meaningful and referential works. We have reported the effect of Al/Si substitution on the structure and luminescence properties of Ca₃SiO₄:Ce³⁺ phosphors [5]. Seshadri’s group reported that the best ingredients of SrₓBa₁₋ₓSiO₄:Eu²⁺ phosphors can be obtained by adjusting the ratio of Sr/Ba [6]. Cheetham’s group reported that the γ-Ca₃SiO₄ phase can be stabilized by doping Al³⁺ [7]. Kim’s group, Fuertes’s group and Lee’s group also reported some interesting work on the orthosilicates based phosphors [8–10].

The study on the energy transfer from sensitizer to activator and the involved color tunable emission are very important for the physical insight of the phosphor materials and the development of the new phosphor systems. It is well known to us that Mn²⁺-doped phosphors show broad band emissions from 550 to 700 nm depending on the crystal field of the host materials. Mn²⁺ and Ce³⁺ ions possess d–d and f–d electron configuration, respectively, and they can act as good candidates as activators in phosphors since they exhibit broadband visible light [11–13]. The energy transfer from...
Ce$^{3+}$ to Mn$^{2+}$ ions has been reported in many systems, for example, Ba$_2$Y$_2$Si$_6$O$_{18}$:Ce$^{3+}$,Mn$^{2+}$ [14], Ca$_3$Y(PO$_4$)$_2$:Ce$^{3+}$,Mn$^{2+}$ [15], CaSrAl$_2$O$_6$:Ce$^{3+}$,Mn$^{2+}$ [16], Y$_2$(Si$_2$O$_5$N)$_2$:Ce$^{3+}$,Mn$^{2+}$ [17], and so on. Caldino reported that the Ce$^{3+}$ to Mn$^{2+}$ energy transfer through an electric dipole–quadrupole interaction mechanism appears to be more probable based on the studies on zinc metaphosphate glasses [18].

To the best of our knowledge, the luminescence properties and energy transfer of Ce$^{3+}$/Mn$^{2+}$ in CaSrSiO$_4$ host have not been reported. In the present work, a series of CaSrSiO$_4$:Ce$^{3+}$,Li$^+$,Mn$^{2+}$ phosphors were synthesized by the solid-state reaction method. We have also investigated its luminescent properties and energy transfer process between the Ce$^{3+}$ and Mn$^{2+}$ ions, as well as the fluorescence lifetime and thermal stability in detail. It is found that the emission color is tunable for the codoped phosphors, which can act as a series of promising phosphors for the wavelength-conversion applications.

2. Experimental procedure

2.1. Materials and synthesis

Ce$^{3+}$ or Mn$^{2+}$ singly doped CaSrSiO$_4$:Ce$^{3+}$,Li$^+$ or CaSrSiO$_4$:Mn$^{2+}$ samples and Ce$^{3+}$ and Mn$^{2+}$ co-doped CaSrSiO$_4$:Ce$^{3+}$,Li$^+$,Mn$^{2+}$ phosphors were all synthesized by the traditional high temperature solid-state technique. Among them, Li$^+$ is added as the charge compensation ion when Ce$^{3+}$ was introduced into the CaSrSiO$_4$ host. The starting materials were as follows: Li$_2$CO$_3$ (A.R.), SrCO$_3$ (A.R.), CaCO$_3$ (A.R.), MnCO$_3$ (A.R.), SiO$_2$ (A.R.) and CeO$_2$ (99.99%). In an agate mortar after grinding and mixing for 40 min, the mixture was placed in a crucible and then sintered at 1400 °C for 4 h in a reducing atmosphere of N$_2$ (90%) and H$_2$ (10%) to produce the final samples. Finally, the prepared phosphors were cooled to room temperature and reground for further measurements.

2.2. Characterization methods

The powder X-ray diffraction (XRD) measurements were performed on D8 Advance diffractometer (Bruker Corporation, Germany) operating at 40 kV and 40 mA with Cu K$_\alpha$ radiation ($\lambda = 1.5406$ Å). The scanning rate for phase identification was fixed at $4^\circ$/min with 2$\theta$ ranges from 10° to 70°. The PL and photoluminescence excitation (PLE) spectra were recorded by a Hitachi F–4600 spectrophotometer (HITACHI, Tokyo, Japan) equipped with a 150 W xenon lamp as the excitation source. The temperature-dependence luminescence properties were also measured on the same spectrophotometer, and it was combined with a self-made heating attachment and a computer-controlled electric furnace (Tianjin Orient KOJI Co., Ltd., TAP-02). The decay curves were recorded on an instrument (Edinburgh Instruments Ltd., U.K., FLSP920), and a n900 flash lamp with the duration of 40 kHz (pulse width: 2.0 ns) was used as the excitation source.

3. Results and discussion

3.1. Phase structure of the samples

Fig. 1 presents the XRD patterns of Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^+$ (i) and Ca$_{0.75}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^+$,0.20Mn$^{2+}$ (ii). The standard data for CaSrSiO$_4$ (JCPDS 72-2260) is shown as a reference.

![Fig. 1. XRD patterns of Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^+$ (i) and Ca$_{0.75}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^+$,0.20Mn$^{2+}$ (ii). The standard data for CaSrSiO$_4$ (JCPDS 72-2260) is shown as a reference.](image)

![Fig. 2. PL spectra of Ca$_{1-x}$Sr$_x$SiO$_4$:xCe$^{3+}$,xLi$^+$ as a function of Ce$^{3+}$ content.](image)

Fig. 2 shows the PL spectra of Ca$_{1-x}$Sr$_x$SiO$_4$:xCe$^{3+}$,xLi$^+$ as a function of Ce$^{3+}$ content. It can be easily seen that the blue emission of the Ce$^{3+}$-doped samples is found to be more probable based on the studies on zinc metaphosphate glasses [18].

Since the Ca$^{2+}$/Sr$^{2+}$ sites in CaSrSiO$_4$ are in disorder state, we cannot draw a conclusion that the doped ions will enter which specific sites; however, the pure phase clearly suggests that the activator and sensitizer have been successfully incorporated in the lattice.

3.2. Photoluminescence properties and energy transfer studies

Fig. 2 shows the PL intensity of the plot of Ca$_{1-x}$Sr$_x$SiO$_4$:xCe$^{3+}$,xLi$^+$ as a function of Ce$^{3+}$ content. It can be easily seen that the blue emission of the Ce$^{3+}$ ions increases gradually and reaches a maximum at $x = 0.10$, then the emission intensity decreases, which could be ascribed to the internal concentration quenching effect. According to the Dexter’s energy transfer theory, at high concentration the nonradiative energy migration among the Ce$^{3+}$ ions may result in the observed concentration quenching. The critical distance between the Ce$^{3+}$ ions may result in the observed concentration quenching.
ions can be calculated using the following equation:

$$R_c = 2 \left( \frac{3V}{4\pi\kappa N} \right)^{1/3}$$

(1)

where $V$ is the volume of a unit cell, $x_c$ is the critical concentration, and $N$ is the number of sites that Ce$^{3+}$ can substitute per unit cell. In our case, $N = 8$, $V$ is estimated to be 370.06 Å$^3$, and $x_c$ is 0.05. The $R_c$ obtained is about 12.09 Å on the basis of the above equation and the corresponding data. As far as we know, the critical distance between the activator and sensitizer is always less than 3–4 Å between the exchange interactions. Thus we can determine the quenching mechanism of Ce$^{3+}$ ions primarily from the case of multi-polar interaction [19,20].

Fig. 3a shows the PLE (left) and PL (right) spectra of Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^{+}$ (a), Ca$_{0.8}$Sr$_{3}$SiO$_4$:0.20Mn$^{2+}$ (b), and Ca$_{0.75}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^{+}$,0.20Mn$^{2+}$ (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4 shows the PL spectra of Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^{+}$,0.20Mn$^{2+}$ (x = 0, 0.15, 0.18, 0.20, 0.25, and 0.30) phosphors under 365 nm excitation. The inset shows the PL spectra of Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^{+}$,0.20Mn$^{2+}$ (x = 0.20, 0.25, and 0.30). Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^{+}$,0.20Mn$^{2+}$ phosphor appears not only as a blue band of Ce$^{3+}$ ions, but also shows a red emission band originated from the Mn$^{2+}$ ions. Therefore, the luminescence color of Ca$_{0.75}$Sr$_{0.95}$SiO$_4$:Ce$^{3+}$,Li$^{+}$,Mn$^{2+}$ can be adjusted by controlling the relative concentrations of Ce$^{3+}$ and Mn$^{2+}$ in CaSrSiO$_4$ host through the energy transfer between them [22].

In order to further understand the energy transfer process involved in the present Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:Ce$^{3+}$,Li$^{+}$,Mn$^{2+}$ system, we synthesized a series of Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:Ce$^{3+}$,Li$^{+}$,Mn$^{2+}$ samples to confirm that. Based on the above results, we fixed the content of Ce$^{3+}$ at the optimum value $x = 0.05$ and the concentration of Mn$^{2+}$ was varied in the range of 0–0.30. Fig. 4 shows the PL spectra of Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^{+}$,0.20Mn$^{2+}$ (x = 0, 0.15, 0.18, 0.20, 0.25, and 0.30) phosphors under 365 nm excitation. Also the inset of Fig. 4 shows the PL spectra of Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^{+}$,0.20Mn$^{2+}$ (x = 0.20, 0.25, and 0.30). We can find that the intensity of Ce$^{3+}$ emission at 450 nm decreased with increasing Mn$^{2+}$ concentration. By comparison, the PL intensity of Mn$^{2+}$ emission increased when the Mn$^{2+}$ concentration reaches the quenching content at $x = 0.20$, and then it decreased. The apparent changes in the emission intensities of Mn$^{2+}$ and Ce$^{3+}$ in Ca$_{0.95}$Sr$_{0.95}$SiO$_4$:0.05Ce$^{3+}$,0.05Li$^{+}$,0.20Mn$^{2+}$ strongly suggest a continuous energy transfer from Ce$^{3+}$ ions to Mn$^{2+}$ ions.

Furthermore, a red-shift behavior originating from Mn$^{2+}$ ions can also be observed with increasing Mn$^{2+}$ content, which could be explained by the variation of crystal field strength around Mn$^{2+}$ ions. A measure of the crystal field strength ($D_c$) around Mn$^{2+}$ ions can be depicted as follows:

$$D_c = \frac{z^2e^2r^4}{6\kappa^2}$$

(2)

where $D_c$ is measurement of the crystal field strength, $z$ is the anion charge, $R$ is the distance between then central ion and its ligands, $r$ is the $d$ wave function radius, and $e$ is the electron charge. As Mn$^{2+}$ ions were introduced into the Ca$_{0.95}$Sr$_{0.95}$SiO$_4$ host, it will occupy the larger Ca$^{2+}$/Sr$^{2+}$ sites. With the increase of Mn$^{2+}$ concentration, the $R$ values in the system decrease, and then it will cause larger $D_c$ values, which makes the enhancement of crystal field strength surrounding Mn$^{2+}$ ions and the lowest 3d state of Mn$^{2+}$ closer to its ground state and finally producing a red-shift of emission peak. Additionally, exchange interaction between Mn$^{2+}$ ion pairs may also cause the redshift [23–25].
On the base of Dexter’s formula of multi-polar interaction, the following relation can be given:

$$\frac{I_0}{I_s} \propto C^{n/3}$$

where $I_s$ and $I_0$ are the luminescence intensities of the sensitizer $\text{Ce}^{3+}$ without and with activator $\text{Mn}^{2+}$ present, and $C$ is the concentration of the sum of $\text{Mn}^{2+}$ and $\text{Ce}^{3+}$. Fig. 5 presents the dependence of $I_0/I_s$ of $\text{Ce}^{3+}$ on (a) $C^{0.3}$, (b) $C^{0.3}$, and (c) $C^{0.3}$. The plots of $(I_0/I_s)$ versus $C^{0.3}$ with $n=10$, $8$, $6$ and correspond to quadrupole–quadrupole (q–q), dipole–quadrupole (d–q) and dipole–dipole (d–d) interactions, respectively. A linear behavior can be observed when $n=8$ and $n=10$. This shows that the energy transfer from $\text{Ce}^{3+}$ to $\text{Mn}^{2+}$ may be a quadrupole–quadrupole interaction or dipole–quadrupole interaction [26]. In order to further analyze the energy transfer interaction mechanism between $\text{Ce}^{3+}$ and $\text{Mn}^{2+}$, the Inokuti–Hirayama model can be used. In the energy transfer process from $\text{Ce}^{3+}$ and $\text{Mn}^{2+}$, the $\text{Ce}^{3+}$ luminescence intensity decay curves can be represented by the formula:

$$I_t(t) = I_{0t}(t) f(t)$$

where $I_{0t}(t)$ is the decay function of $\text{Ce}^{3+}$ without $\text{Mn}^{2+}$, $f(t)$ is due to the energy transfer to $\text{Mn}^{2+}$ from excited $\text{Ce}^{3+}$. The energy transfer rate between $\text{Ce}^{3+}$ and $\text{Mn}^{2+}$ is inversely proportional to the distance, $f(t)$ can be obtained by the following formula:

$$f(t) = \exp \left\{ -\frac{4}{3} \alpha \Gamma \left(1 - \frac{m}{3}\right) \frac{n_a}{n_a + n_b} \right\}$$

where $\alpha$ is the rate constant for energy transfer, $m=10$, $8$, $6$ correspond to quadrupole–quadrupole (q–q), dipole–quadrupole (d–q) and dipole–dipole (d–d) interactions, respectively, $n_a$ is the number of acceptor number in per unit volume. By Eqs. (4) and (5) we can know $\log[(\ln[I(t)]/\ln[I(0)])] and $I(t)$ has a linear function with a slope of $3/m$. The experimental data plots of $\log[\ln(I(t))/\ln(I(0))]$ versus $\log(t)$ of $\text{Ce}^{3+}$ in $\text{Ca}_{0.75}\text{Sr}_{0.25}\text{SiO}_4:0.05\text{Ce}^{3+},0.05\text{Li}^{3+}$. $0.20\text{Mn}^{2+}$ and the fitting result are shown in Fig. 6. From the calculated slope of the fitting line, the value of $m$ can be estimated to be $7.14$ for $\text{Ca}_{0.75}\text{Sr}_{0.25}\text{SiO}_4:0.05\text{Ce}^{3+},0.05\text{Li}^{3+}$. $0.20\text{Mn}^{2+}$ phosphor. Accordingly, in $\text{CaSrSiO}_4$ host the dipole–quadrupole interaction predominates in the energy transfer mechanism from $\text{Ce}^{3+}$ to $\text{Mn}^{2+}$ ions [27].

Moreover, the decay time of $\text{Ce}^{3+}$ in $\text{CaSrSiO}_4:0.05\text{Ce}^{3+}$ $\text{Li}^{3+}$ $\text{Mn}^{2+}$ phosphors were measured under excitation at $365$ nm and monitored at $450$ nm. The decay curves of $\text{Ce}^{3+}$ emission in $\text{Ca}_{0.95-}0.05\text{Sr}_{0.95}$ $\text{SiO}_4:0.05\text{Ce}^{3+},0.05\text{Li}^{3+}$. $\text{Mn}^{2+}$ phosphors, are shown in Fig. 7. It can be seen that the decay curves of the $\text{CaSiSiO}_2$ $\text{Ce}^{3+}$ $\text{Li}^{3+}$. $\text{Mn}^{2+}$ phosphors can be well fitted with a second-order exponential decay, as discussed in our previous work [5]. Therefore, the decay time of $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{SiO}_4:0.05\text{Ce}^{3+},0.05\text{Li}^{3+}$ sample was determined to be $39.61$ ns. However, the decay of $\text{Ce}^{3+}$ ions significantly deviates from the second-exponential decay with the $\text{Mn}^{2+}$. Since, the decay processes of $\text{CaSrSiO}_4:0.05\text{Ce}^{3+},0.05\text{Li}^{3+},0.20\text{Mn}^{2+}$ samples are characterized by average lifetime ($\tau$), which was defined by the formula as follows:

$$\tau = \frac{\int_0^\infty l(t) dt}{\int_0^\infty l(t) dt}$$

where $l(t)$ stands for the intensity at time $t$. Based on Eq. (6), the lifetimes value of $\text{Ce}^{3+}$ were calculated to be $36.1$, $34.5$, $32.1$ and $29.5$ ns for $\text{Ca}_{0.95-}0.05\text{Sr}_{0.05}\text{SiO}_4:0.05\text{Ce}^{3+},0.05\text{Li}^{3+},0.20\text{Mn}^{2+}$ phosphors with $x=0.05, 0.10, 0.15$ and 0.20, respectively. The decay time was found to decrease with an increasing $\text{Mn}^{2+}$ dopant content, which demonstrates the energy transfer process occurs from $\text{Ce}^{3+}$ to $\text{Mn}^{2+}$. Furthermore, the energy transfer efficiency ($\eta$) between $\text{Ce}^{3+}$ and $\text{Mn}^{2+}$ ions in $\text{CaSrSiO}_4$ matrix was also determined from the decay lifetime by using the equation...
Thermal stable luminescence and the CIE diagram

Fig. 9 presents the temperature dependent emission spectra of Ca_{0.95}Sr_{0.05}SiO_{4}:0.05Ce^{3+},0.05Li^{+},0.20Mn^{2+}. The inset shows the relative intensity on working temperature. It can be seen that at 150 °C the emission intensity of the Ca_{0.75}Sr_{0.20}SiO_{4}:0.05Ce^{3+},0.05Li^{+},0.20Mn^{2+} phosphor is about 72.3% of that measured at room temperature. Also with increasing temperature, the emission band of Mn^{2+} ions shows a blueshift whereas the emission band position for Ce^{3+} ions stays unchanged. Usually, the phonon-coupling may cause the blueshift of emission spectrum, in which the electrons are tuned from a low energy level to a higher energy level, electron transit from the high excited level to the ground state then radiate light. We also can find a similar phenomenon in other phosphors doped with Mn^{2+} ions. This result proves that CaSrSiO_{4}:Ce^{3+},Li^{+},Mn^{2+} phosphors have good thermal stability.

The CIE chromaticity diagram is presented in Fig. 10, and the corresponding coordinates of the selected Ca_{0.95}Sr_{0.05}SiO_{4}:0.05Ce^{3+},0.05Li^{+},xMn^{2+}. (x=0, 0.15, 0.20, and 0.25) phosphors (λ_{ex}=365 nm) are calculated and marked in Fig. 10 and also listed in Table 1. Moreover, the digital photographs of the selected phosphors upon 365 nm UV lamp extraction are presented in Fig. 10. The inset in Fig. 10 presents the typical color emission spectra of the selected Ca_{0.95}Sr_{0.05}SiO_{4}:0.05Ce^{3+},0.05Li^{+},xMn^{2+}. (x=0, 0.15, 0.20, and 0.25) phosphors, respectively. It can be clearly seen the Ce^{3+} emission and the Mn^{2+} red emission spectra in the corresponding composition [31,32]. Meanwhile, the CIE chromaticity coordinate can be modulated from (0.156, 0.106) to (0.219, 0.211), which result from the variation of the emission intensity of Mn^{2+} and Ce^{3+} through the energy transfer from Ce^{3+} to Mn^{2+} ions. By adjusting Mn^{2+} doped contents, the emission color can be tunable.

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in wLEDs and functional sunlight spectrum conversion device [33,34].

4. Conclusions

In conclusion, a series of color tunable CaSrSiO$_4$:Ce$^{3+}$,Li$^+$,Mn$^{2+}$ phosphors have been prepared through a conventional solid-state reaction. The as-obtained phosphors have a broad excitation band ranging from 250 to 450 nm. The spectroscopic data and fluorescence decay dynamics demonstrate that the energy transfer from Ce$^{3+}$ to Mn$^{2+}$ is ascribed to a dipole-quadrupole interaction. CaSrSiO$_4$:Ce$^{3+}$,Li$^+$,Mn$^{2+}$ phosphor had a good thermal stability, and the emission intensity at 150 °C can keep 72.3% of that measured at room temperature. The CIE chromaticity coordinate can be modulated from (0.156, 0.106) to (0.224, 0.211) by controlling the doping content of the Mn$^{2+}$ ions with the fixed Ce$^{3+}$ content. All of the above results indicate that CaSrSiO$_4$:Ce$^{3+}$,Li$^+$,Mn$^{2+}$ phosphors may be potential in wLEDs and functional sunlight spectrum conversion device.

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References