Research Article

Synthesis of Blue-Green Phosphors Sr₄Si₃O₈Cl₄:Eu²⁺ by Gel-Combustion Method and Their Luminescent Properties

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Sr₄Si₃O₈Cl₄:Eu²⁺ blue-green phosphors were synthesized by the gel-combustion method. The as-synthesized phosphors were analyzed and characterized by X-ray diffraction and fluorescence spectrophotometer. The results indicate that orthorhombic phase Sr₄Si₃O₈Cl₄:Eu²⁺ has been formed after the precursor calcined at 900 °C reductive temperature. The excitation spectrum of Sr₄Si₃O₈Cl₄:Eu²⁺ is a broad band in the range of 250 ~ 450 nm and the main peak at 324 nm. The emission spectrum is also a broadband with the main emission peak at about 484 nm, which is ascribed to the typical 4f⁵5d¹→4f⁷ transition of Eu²⁺.

Moreover, the effects of the concentration of Eu²⁺, the reductive temperature, and the doping amount of Mg²⁺ on luminescent properties were discussed.

1. Introduction

White light emitting diodes (LED) have been paid more and more attention due to their high efficiency, little volume, long service life, mercury pollution-free, and energy conversation [1–5]. The properties of phosphors as supporting materials have great effect on the luminescence efficiency, the brightness, and Ra of white LED. The phosphors for white LED should meet the following requirements. First, the phosphors can be excited effectively by ultraviolet (UV), near-ultraviolet (NUV) or blue light, and emit visible light. Second, the phosphors should have excellent temperature quenching properties. Third, the phosphors possess stable physical and chemical properties. Fourth, the particle size of the phosphors is moderate and the particle are well dispersed [6].

Alkali earth halide and silicate compound are both effective host as the Eu²⁺ luminescence matrices. As the multiplex compound, alkali earth chlorosilicate crystal has lower synthesis temperature and higher physical chemistry stability [7]; it is easy access to the effective excitation from UV-NUV band, so it is used widely in varieties of displays and lighting equipments. In the chlorosilicate host, the luminescence of Eu²⁺ consists of a 4f⁵5d¹→4f⁷(⁸S₇/₂) broad-band emission, which belongs to electric-dipole allowed transition and has the properties of large absorption of UV-NUV band light and broad emission range from ultraviolet to infrared light depending on different crystal-lattice environment.

We have developed a new kind of synthesis method, that is, the gel-combustion method, for the synthesis of silicate luminescent materials [8, 9]. This method has several advantages, including low calcination temperature, short calcination time, easy operation, the uniformity of product ingredients, and small particles with good dispersity. In our present work, Sr₄Si₃O₈Cl₄:Eu²⁺ phosphors were synthesized by the gel-combustion method. The phase structure of the samples obtained at different reductive temperature is analyzed by XRD, and the luminescent mechanism of Eu²⁺ in Sr₄Si₃O₈Cl₄ host is discussed by analyzing the excitation and emission spectra. Furthermore, the effects of the concentration of Eu²⁺, the reductive temperature and the doping amount of Mg²⁺ on luminescent properties were studied.
2. Experimental

2.1. Synthesis. Sr(NO₃)₂, Mg(NO₃)₂ · 6H₂O, SrCl₂ · 6H₂O, (C₂H₅O)₄Si (TEOS), Eu₂O₃, CO(NH₂)₂ (Urea), anhydrous ethanol, and HNO₃ were employed as raw materials. They were all analytical reagents (A.R.).

The goal products Sr₄Si₃O₈Cl₄:Eu²⁺ were prepared by gel-combustion method. The procedure is as follows. First, Eu₂O₃ was dissolved in appropriate nitric acid to prepare Eu(NO₃)₃ solution, and then the accurate concentration was determined by ethylenediaminetetraacetic acid disodium salt (EDTA) complexing titration to ensure the desired stoichiometry. A certain volume of solvent anhydrous ethanol was added into a 100-mL ceramic crucible. According to the nominal composition of Sr₄Si₃O₈Cl₄:Eu²⁺, stoichiometric Si(OC₂H₅)₄, Sr(NO₃)₂, SrCl₂-6H₂O, Eu(NO₃)₃, solution, and appropriate amounts of urea and distilled water were added in order. The mixture was stirred to obtain a homogenous and transparent solution. Subsequently, a small amount of HNO₃ was added as a catalyst and the pH value of the solution was adjusted to 2 ~ 3. Next, the resulting solution was heated by water bath at 70°C to evaporate superfluous water. The volume of the solution decreased and the viscosity increased continuously because of gradual polymerization. When the volume of the solution could not decrease, the solution became a transparent gel. Then the gel was put into oven and dried at 70°C. The dry gel was ignited on an electric stove in air atmosphere. This combustion process only took about 2 min. A dry white sponge sample (which was called the precursor) was formed. Due to the evolved gases, the apparent volume expanded after combustion and the precursor became so loose that it could be broken into fine pieces easily. Finally, the precursor was calcined in a muffle furnace under an active carbon atmosphere at a temperature of 700~1000°C for 3 h to obtain the sample.

2.2. Characterization. Phases and crystallization of the samples were identified by X-ray diffraction analysis (XRD) with a Y-2000 diffractometer using Cu-Kα radiation (30 kV × 20 mA, and a scanning speed 0.06°/s). The excitation and emission spectra of the samples were recorded on an F-380 fluorescence spectrometer. All measurements were carried out at room temperature.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis. Figure 1 shows the typical XRD patterns of as-synthesized samples obtained from the precursor at the different reductive temperature for the same reductive time (3 h) by gel-combustion method.

From Figure 1, it can be seen that the XRD pattern of sample obtained at a reductive temperature of 700°C has a higher background and the lower intensity of the diffraction peak, which indicates that the sample still belongs to amorphous. When the reductive temperature is increased to 800°C, the diffraction data of the sample is basically consistent with that of Sr₄Si₃O₈Cl₄ (JCPDS no. 40-0074), which indicates that Sr₄Si₃O₈Cl₄:Eu²⁺ has formed at a reductive temperature of 800°C, gel-combustion method can reduce effectively the temperature of the phase formation, but a little amount of SrSiO₃ (JCPDS no. 34-0099) can be found. So, it is necessary to increase the reductive temperature in order to further improve the purity of the phase. As shown in Figure 1, for the sample obtained at 900°C, the diffraction peaks corresponding to Sr₄Si₃O₈Cl₄ become stronger and sharper, while the diffraction peaks corresponding to SrSiO₃ become weaker obviously, so appropriately raising the reductive temperature can improve the purity of the phase and make the sample crystallize better. But when the reductive temperature is increased to 950°C ~ 1000°C, the intensity of the diffraction peaks of Sr₄Si₃O₈Cl₄ decreases significantly, and the intensity of the diffraction peaks of SrSiO₃ increases remarkably. Therefore, overhigh reductive temperature is against the formation of pure Sr₄Si₃O₈Cl₄.

Owing to the same charge and similar radius of Eu²⁺ and Sr²⁺, the doped Eu²⁺ ions have little effect on crystal structure of the host Sr₄Si₃O₈Cl₄. Sr₄Si₃O₈Cl₄:Eu²⁺ also belongs to orthorhombic crystal structure as that of Sr₄Si₃O₈Cl₄.

3.2. Excitation Spectrum and Emission Spectrum of Sr₄Si₃O₈Cl₄:Eu²⁺. Figure 2 shows the excitation and emission spectra of Sr₄Si₃O₈Cl₄:Eu²⁺ obtained at 900°C reduction temperature. It can be seen from Figure 2(a), the excitation spectrum show a broad band from 250 to 450 nm (monitored at 484 nm), and the main peak is at about 324 nm, which is attributed to the typical excitation of Eu²⁺ (d-f transition). The excitation spectrum of Sr₄Si₃O₈Cl₄:Eu²⁺ covers a wide region between 250 and 450 nm, therefore the phosphors can be excited by UV and NUV effectively and can match well with UV- and NUV-LED, showing a great potential for practical applications. Under UV irradiation at 324 nm,
Sr$_4$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$ shows a broad-band emission (shown in Figure 2(b)). It is ascribed to the typical transition 4f$^5$5d$^1$ → 4f$^5$ of Eu$^{2+}$. The main emission peak is at about 484 nm, so the phosphor gives a strong blue-green luminescence.

According to the report of Van Uttert [10], for most divalent and some trivalent rare earth ions in suitable matrices, such as sulfide, oxide, halide and aluminates, the following experiential equation gives a good fit to the emission peak and 5d excitation edge data for Eu$^{2+}$ and Ce$^{3+}$:

$$E = Q \left[1 - \left(\frac{V}{V_0}\right)^{1/3} \right]^{-\frac{1}{10-\left(nA_r\right)/80}} \quad \text{(cm}^{-1}\text{)}.$$  

(1)

In (1), $E$ represents the position of the d-band edge in energy for rare earth ions (cm$^{-1}$); $Q$ is the position in energy for the lower d-band edge for the free ion; the value of $Q$ is 34,000 cm$^{-1}$ for Eu$^{2+}$; $V$ is the valence of the “active” cation, here $V = 2$; $n$ is the number of anions in the immediate shell about this ion; $A$ is the electron affinity of the atoms that form anions, here $A$ is regard as 2.19 eV in Sr$_4$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$; $r$ is the radius of the host cation replaced by the “active” cation. According to X-ray diffraction data reported by Wang et al. [11], it is confirmed that Sr$^{2+}$ is coordinated by four O atoms and four Cl atoms in the Sr$_4$Si$_3$O$_8$Cl$_4$ host and the sites of Sr$^{2+}$ can be substituted by Eu$^{2+}$ in the Sr$_4$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$ phosphor, whichever factor like radius and charge is considered. So the value of coordination number of Eu$^{2+}$ is eight, and the radius of Sr$^{2+}$ under this coordination environment is 0.126 nm. Based on the above-mentioned equation and the data, the value of $E$ is calculated as 21,264 cm$^{-1}$, which corresponds to an emission-peak wavelength of 470 nm of Eu$^{2+}$ in Sr$_4$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$. As shown in Figure 2, Sr$_4$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$ exhibits an emission-peak wavelength of 484 nm, corresponding to 21,943 cm$^{-1}$ in energy, which has little difference from the theoretical value 21,264 cm$^{-1}$, and the difference can be due to the variation of crystal field and covalence strength.

3.3. Effect of Eu$^{2+}$ Concentration on the Luminescence Properties of Samples. In order to investigate the effect of Eu$^{2+}$ concentration ($x$) on luminescent properties of the samples, a series of samples Sr$_{4-x}$Si$_3$O$_8$Cl$_4$:Eu$_x$$^{2+}$ ($x = 0.01 \sim 0.14$) were synthesized and their emission spectra are shown in Figure 3. It can be seen that the Eu$^{2+}$ concentration has little effect on the shape and position of emission peaks, but has great effect on the intensity. When $x$ varies in the range of 0.01~0.06, the intensity of emission peaks at 484 nm increases gradually with the increase of Eu$^{2+}$ concentration and reaches the maximum when the concentration ($x$) of Eu$^{2+}$ is 0.06. Concentration quenching occurs when $x$ is beyond 0.06, that is, the luminescent intensity decreases with the increase of Eu$^{2+}$ concentration. The reason is that the phosphor has less luminescent centers when Eu$^{2+}$ concentration is relatively low, thereby the luminescent intensity is weak; with the increase of Eu$^{2+}$ concentration, luminescent centers increase, the energy absorbed by Eu$^{2+}$ increases, so the luminescent intensity is enhanced, and Eu$^{2+}$ ions will be close to each other with the increase of Eu$^{2+}$ concentration; the interaction between Eu$^{2+}$ ions is enhanced and the energy transfer is accelerated. When the rate of energy transfer between Eu$^{2+}$ ions is equal to the light emission rate of Eu$^{2+}$, the luminescent intensity of Eu$^{2+}$ reaches the maximum. Since then, with the further increase of Eu$^{2+}$ concentration, the energy transfer rate between Eu$^{2+}$ ions will rapidly increase and exceed the light emission rate of Eu$^{2+}$; Eu$^{2+}$ has not been able to emit light but energy transfer has happened. So the excitation energy is consumed by crystal lattice transfer, leading to the decrease of emission intensity, that is, the concentration quenching effect occurs [12]. So, Eu$^{2+}$ concentration has an optimum value; for Sr$_{4-x}$Si$_3$O$_8$Cl$_4$:Eu$_x$$^{2+}$, the optimum concentration of Eu$^{2+}$ is 0.06 ($x = 0.06$).

According to the theory of concentration quenching in inorganic phosphors proposed by Dexter and Schulman [13], the relationship between the luminescent intensity after the emergence of concentration quenching and the concentration of activator can be obtained as follows:

$$I \propto x^{1-s/3},$$  

(2)

where $I$ represents the luminescent intensity of phosphors; $x$ is the doping concentration of activator; $s$ is the index of electric multipole interaction. Based on (2), it can be deduced that the slope of the relation curve ($\lg(I/x) - \lg x$) in the double logarithm coordinates is $-s/3$. When $s = 6, 8$, and 10, the concentration quenching is caused, respectively, by electric dipole-dipole (d-d) interaction, electric dipole-quadrupole (d-q) interaction, and electric quadrupole-quadrupole (q-q) interaction.

Figure 4 shows the concentration dependence curves ($\lg(I/x) - \lg x$) for Sr$_{4-x}$Si$_3$O$_8$Cl$_4$:Eu$_x$$^{2+}$ when Eu$^{2+}$ doping concentration is more than the optimum concentration ($x = 0.06$). By linear fitting to the experimental points in Figure 4, it is found that the slope is $-2.16$. From the slope, the value of $s$ can be calculated, and $s = 6.48$, which is close to 6, therefore Eu$^{2+}$ concentration quenching in Sr$_{4-x}$Si$_3$O$_8$Cl$_4$:Eu$_x$$^{2+}$ is mainly due to d-d interaction.

3.4. Effect of Reductive Temperature on the Luminescence Intensity of Samples. Taking into account that too low reductive temperature is not favorable to form single phase, the crystallization of material may not be complete, and overhigh temperature can lead to hard aggregate or glass state and even causes the destruction of the material during grounding and milling, which will result in the significant decrease of luminescence intensity of the phosphors. So, the effect of reductive temperature on luminescence intensity of Sr$_4$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$ in the range of 700°C~1000°C was investigated. Figure 5 shows the emission spectra of the samples obtained at different reductive temperature (while other conditions are fixed).

It can be seen from Figure 5 that the reductive temperature has great effect on the intensity of emission peak. The intensity of emission peak is enhanced significantly with the temperature increasing in the range of 700°C~900°C. It is
becausethatthecrystallizationofthesampleandphasepurity areimprovedwiththeincreaseofthereductivetemperature (verified by Figure 1). When the reductive temperature is 900°C, the intensity of emission peak is the highest. But when the reductive temperature is in the range of 950 ~ 1000°C, the intensity of the emission peak is reduced significantly with the increase of the reductive temperature. The reason is that the crystal structure of the sample has been changed when reductive temperature is above 950°C, as shown in Figure 1, Sr4Si3O8Cl4 has been transformed into SrSiO3, and Eu2+ cannot glow efficiently in SrSiO3 host, thus resulting in the greatly decrease of luminescence intensity of the phosphor. Therefore, 900°C is the suitable reductive temperature.

3.5. Effect of Mg2+ Concentrations on Sr4Si3O8Cl4: Eu2+ Luminescence Intensity. As an activated ion, Eu2+ ion with the 5d electron is unshielded from the crystal field by the 5s and 5p electron, and the different intensity of the crystal field leads to the different splitting of the 5d energy levels. The spectral properties of Eu2+ are strongly affected by the surrounding environment like symmetry, covalence, coordination, bond length, site size, and crystal-field strength [14]. So the Eu2+ has the properties of strong absorption of UV light and broad emission range from ultraviolet to infrared light depending on different crystal-lattice environment.

By changing the doping amount of Mg2+, a series of Sr4-xMg2+xSi3O8Cl4: Eu2+ (x = 0, 0.1, 1.5, 2.0) phosphors were successfully synthesized under the condition of invariable concentration of Eu2+ in the host lattice. The excitation and
emission spectra of the samples are shown in Figure 6. It can be seen from Figure 6(a) that all the excitation spectra of the samples show characteristic excitation spectra bands of Eu$^{2+}$, which is broad in the range from 250 nm to 450 nm. But the position of main excitation peak has been changed. When the doping amount of Mg$^{2+}$ ($x$) increases from 0 to 2.0, the main excitation peak shifts from 324 nm to 343 nm. From Figure 6(b), it can be seen that the position of the emission peak moves from 484 nm to 436 nm with the doping amount of Mg$^{2+}$ ($x$) increasing from 0 to 2.0, thus the color of the phosphors under UV or NUV radiation changes from blue-green to blue. The blue shift of emission peaks is due to the decrease of crystal field strength when Mg$^{2+}$ ions replace Sr$^{2+}$ ions, which makes the crystal field splitting of 5d energy levels of Eu$^{2+}$ decreases, and 4f$^6$ 5d$^1$ state of Eu$^{2+}$ moves to high-energy level, so it results in the blue shift of emission peak.

In addition, it can be seen from Figure 6 that the intensity of the excitation and emission peaks are enhanced remarkably by the increase of Mg doping amount in Sr$_{4-x}$Mg$_x$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$ ($x = 0, 1.0, 1.5, 2.0$).

Xia et al. [7] synthesized Sr$_{4-x}$Mg$_x$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$ ($x = 0, 0.5, 1.0, 1.5$) by the high temperature solid-state method at 950°C for 4 h using carbon powder as reducing agent. The position of the emission peak moved from 496 nm to 467 nm with the doping amount of Mg$^{2+}$ ($x$) increasing from 0 to 1.5, and the intensity of emission peak decreased with the increase of Mg doping amount. Zhang et al. [15] synthesized Sr$_{4-x}$Mg$_x$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) by a general high temperature solid-state reaction at 900°C for 4 h under a carbon monoxide reductive atmosphere. The position of the emission peak did not change with the doping amount of Mg$^{2+}$ ($x$), all the emission peaks are at about 484 nm, and the intensity of emission peak first increased with the increase of Mg doping amount; the emission intensity is up to the highest when $x = 0.5$, then decreased. Therefore, our experiment results are different from those reported by Xia et al. [7] and Zhang et al. [15]. The reason may be due to different microstructure and crystal-lattice environment caused by different synthesis method.

4. Conclusions

In this work, blue-green phosphor Sr$_x$Si$_3$O$_8$Cl$_4$:Eu$^{2+}$ with orthorhombic crystal structure were successfully synthesized by the gel-combustion method. The phosphors are suitable
to be excited by an UV- or NUV-emitting LED chip due to their broad excitation band extending from 250 nm to 450 nm, showing good prospect for blue-green phosphors of white LED. The optimum concentration of Eu$^{2+}$ ($x$) is 0.06 in \( \text{Sr}_{x} \text{Si}_4 \text{O}_{8} \text{Cl}_4 \cdot \text{Eu}^{2+} \cdot 2\text{H}_2\text{O} \). Concentration quenching occurs when $x$ is beyond 0.06, which is mainly due to electric dipole-dipole interaction. The appropriate reductive temperature is 900 $^\circ$C in order to improve the purity of the phase and make the sample crystallize better. Codoping Mg$^{2+}$ in Sr$_3$Si$_4$O$_8$Cl$_4$:Eu$^{2+}$ makes the emission peak shift from 484 nm to 436 nm and greatly enhances the intensity of the emission peak. So, Mg$^{2+}$ is an ideal codoped ion for modulating color and improving luminescent intensity of Sr$_3$Si$_4$O$_8$Cl$_4$:Eu$^{2+}$ phosphors.

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