Study on Preparation and Luminescence Properties of Li$_2$CaSiO$_4$: Pr$^{3+}$ Phosphor

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Abstract. In this paper, a high-temperature solid-phase method was used to synthesize Pr$^{3+}$ ion-doped Li$_2$CaSiO$_4$ matrix phosphor. An X-ray diffractometer and a fluorescence transient spectrometer were used to characterize the crystal structure and luminescence properties of the prepared phosphors. The results show that the prepared sample is a single phase of Pr$^{3+}$-doped Li$_2$CaSiO$_4$; it exhibits a good orange light emission under the excitation of blue light, and is expected to be used as white light LED lighting.

1. Introduction

In the daily life of modern people, white LED lighting has successfully replaced other lighting methods mainly due to its small size, pollution-free, energy-saving and other advantages. It is known as the fourth-generation lighting system and has become a necessity for human production and life. There are currently three mainstream white LED production methods [1-3]: The first is to use a near-ultraviolet chip to excite red, green, and blue phosphors, which are mixed and matched to form white light; the second is to use a blue chip with a blue excited yellow Phosphor, the remaining blue light is mixed with the excited yellow light to form a white light source; the third is to directly use a combination of red light chip, green light chip, and blue light chip to mix white light.

The second method is still the mainstream form of white LED production on the market, but this combination method has serious shortcomings of low color rendering and high color temperature [4]. To solve this problem, a suitable and efficient red or orange phosphor can be added to the yellow phosphor as a compensation powder to improve the color rendering of white light and reduce the color temperature [5]. This paper uses Li$_2$CaSiO$_4$ as the matrix and rare earth element Pr$^{3+}$ ions as the activation center to prepare Li$_2$CaSiO$_4$:Pr$^{3+}$ orange phosphors by high-temperature solid-phase method, and conduct phase analysis and related optical performance characterization of the prepared samples. Through research, it is found that it is a potential orange phosphor that can be used for white LED lighting.

2. Experimental sections

2.1. Experimental chemical reagents and instruments

The chemical reagents used in the experiment are Li$_2$CO$_3$, CaCO$_3$, SiO$_2$ and Pr$_6$O$_{11}$, all of which are analytically pure. They were purchased from Tianjin Guangfu Fine Chemical Research Institute, Chengdu Kelong Chemical Reagent Factory, Tianjin Fengchuan Chemical Reagent Technology Co., Ltd., Bao
tou Huamei Rare Earth Tech Co., Ltd. The equipment used in the experiment is the FA2204B electronic balance produced by Shanghai Jingke Tianmei Scientific Instrument Co., Ltd., the GHA 12/300 muffle furnace produced by the British Carbolute Company, and the steady-state transient fluorescence spectrometer FS5 produced by the British Edinburgh Instrument Company. And the DX-2700 X-ray diffractometer produced by Dandongfangyuan Instrument Co., Ltd. of the People's Republic of China.

2.2. Preparation
According to certain proportion weighing Li2CO3, CaCO3, SiO2, Pr6O11, Pr3+ doped molar concentration were 0.1%, 0.5%, 1%, 1.5%, 2%), place the raw material in the agate mortar fully grinding, mixing, and then put into corundum crucible, then put corundum crucible in a muffle furnace, in the air, the calcination temperature rise to 700 ℃, keep 1 h, and then calcination temperature rose to 850 ℃, and keep 3 h. After the calcined sample is naturally cooled to room temperature, it is then put into agate mortar to fully grind, and then the experimental sample is obtained. All the samples prepared are white powder.

2.3. Characterization
At room temperature, use X-ray powder diffractometer to detect the phase of the sample, and set the parameters as follows: copper target (Cu target Kα=0.15406nm), tube voltage 40kV, tube current 50mA, scanning range (2θ) Is 20°~90°, and the scanning step is 0.02°; the excitation spectrum and emission spectrum of the sample are characterized by a steady-state transient fluorescence spectrometer FS5 equipped with a xenon lamp as the excitation light source.

3. Results and discussion

![Graph](image)

Figure 1. The XRD diffraction pattern of Li2CaSiO4: xPr3+ (x=0.001, 0.005, 0.01, 0.015, 0.02) phosphor and standard card PDF#27-0290.

3.1. Phase
Figure 1 is the XRD diffraction pattern of Li2CaSiO4: xPr3+ (x=0.001, 0.005, 0.01, 0.015, 0.02) phosphor and standard card PDF#27-0290. It can be clearly seen that the XRD diffraction patterns of Li2CaSiO4: xPr3+ phosphors with different doping concentrations are in good match with the standard card diffraction pattern of Li2CaSiO4 matrix (PDF#27-0290), and the diffraction peaks have no obvious shift. It shows that the main body of the prepared sample is a single phase of Li2CaSiO4, and the doping of Pr3+ ions does not cause a change in the lattice structure of the matrix.
3.2. Luminescence properties

![Excitation spectrum and emission spectra of Li$_2$CaSiO$_4$:0.01Pr$^{3+}$ phosphor](image)

**Figure 2.** Excitation spectrum of Li$_2$CaSiO$_4$: 0.01Pr$^{3+}$ phosphor under excitation wavelength of 619nm and emission spectra of Li$_2$CaSiO$_4$: 0.01Pr$^{3+}$ phosphors under different excitation wavelengths.

The excitation and emission spectra of the phosphor Li$_2$CaSiO$_4$:0.01Pr$^{3+}$ measured at room temperature are shown in Figure 2, respectively. The excitation spectrum is mainly located between 440–500nm, the main excitation peaks are located at 449nm, 477nm, 488nm, which are all narrow bands, and belong to the Pr$^{3+}$ ions' $^3H_4\rightarrow^3P_2(449nm)$, $^3H_4\rightarrow^3P_1(477nm)$, $^3H_4\rightarrow^3P_0(488nm)$ transition, in which
the excitation peak at 488nm is the strongest, and the excitation peak at 449nm is relatively weak; the emission spectrum is mainly between 520~750nm, at 531nm, 598nm, 602nm, 619nm, 627nm, 651nm, 685nm, 709nm, 735nm, respectively, attributable to the transitions of Pr$^{3+}$ ions' $^3P_1$ to $^3H_5(531nm)$, $^3P_1$ to $^3H_6(598nm)$, $^1D_2$ to $^3H_4(602nm)$, $^3P_0$ to $^3H_4(619nm)$, $^3P_1$ to $^3F_2(627nm)$, $^3P_0$ to $^3F_2(651nm)$, $^1D_2$ to $^3H_4(685nm)$, $^3P_1$ to $^3F_4(709nm)$, $^3P_0$ to $^3F_4(735nm)$ [6]. among them, the Li$_2$CaSiO$_4$ matrix phosphor with Pr$^{3+}$ ions doping concentration of 1% has the highest emission peak intensity at 619nm. At the same time, it can be seen that the emission peaks at 619nm and 709nm have obvious splitting, which may be caused by the stark level splitting of the corresponding energy level under the action of the crystal field. For the fluorescence emission spectra under different excitation wavelengths, the emission peak shape has basically not changed much, but under the excitation wavelength of 488nm, the fluorescence emission intensity is slightly stronger.

It can be seen from the excitation spectrum that the doping of Pr$^{3+}$ ions changes from low concentration to high concentration in Figure 3. The emission peak intensity at 598nm, 602nm gradually weakens, and the emission peak intensity at 531nm, 619nm, 651nm, 735nm gradually increases to reach the quenching concentration ($x=0.01$) and then gradually weakened. And it can be clearly seen that when the Pr$^{3+}$ doping concentration is increased from 0.1% to 0.5%, the shape of the emission peak in the range of 580nm~640nm changes significantly. This is because [7]: when the Pr$^{3+}$ doping concentration is low, the photons that are excited to transition to the high-energy state are more inclined: part of the photons directly transition to the low-energy state by means of $^3P_1$→$^3H_6$ (598nm) radiation transition, and the other part is through the $^3P_1$→$^3H_4$ $^1D_2$ $^3H_6$ cross-relaxation method increases the number of photons on the $^1D_2$ energy level, and then continues to the low energy state by means $1D_2$→$^1D_4$ (602nm) radiation transition; when the Pr$^{3+}$ doping concentration is relatively high, the photon in the high energy state is more inclined to the downward transition of the $^3P_0$ energy state, which mainly produces visible light emission, it is mainly through $^3P_0$→$^3H_6$ (619nm), $^3P_0$→$^3F_2$ (651nm), $^3P_0$→$^3F_4$ (735nm) direct radiation transition to reach the low energy state.
Figure 4. Fluorescence lifetime of Li$_2$CaSiO$_4$: xPr$^{3+}$ phosphors with different doping concentrations.

Figure 4 shows the fluorescence decay curve of Li$_2$CaSiO$_4$: xPr$^{3+}$ samples under excitation at 488nm. The doping concentrations of Pr$^{3+}$ are 0.1%, 0.5%, 1%, 1.5%, and 2%, respectively. The double exponential function fitting is performed on the fluorescence curve of the sample to obtain the fluorescence lifetime of samples with different concentrations.

Table 1. Fluorescence lifetime and fitting error of Li$_2$CaSiO$_4$: xPr$^{3+}$ sample under 488nm excitation.

| Doping concentration (%) | Fluorescence lifetime (ns) | Fitting error |
|--------------------------|---------------------------|---------------|
| 0.1                      | 423.6                     | 1.279         |
| 0.5                      | 2494.7                    | 1.199         |
| 1                        | 2434.4                    | 1.273         |
| 1.5                      | 2414.9                    | 1.127         |
| 2                        | 2325.9                    | 1.226         |

Because the Pr$^{3+}$ doping molar concentration is 0.001 and 0.01, the emission peak shapes of the two are quite different. Using the CIE color coordinate calculation software, the CIE color coordinates of Li$_2$CaSiO$_4$: xPr$^{3+}$ phosphors were calculated when the Pr$^{3+}$ doping molar concentration was 0.001 and 0.01, and the excitation wavelength was 488nm. The results show that under the excitation of 488nm blue light, the color coordinates of the two are (0.6039, 0.3942) and (0.5726, 0.4227), respectively, and their luminescence is in the orange light region.

4. Conclusion
In this paper, Li$_2$CaSiO$_4$: xPr$^{3+}$ phosphor was synthesized by high temperature solid phase method. The excitation peak of the phosphor is mainly in the blue range, and the emission peak is mainly in the orange-red range. The main excitation peaks are narrow bands at 449 nm, 477 nm, and 488 nm, and the main strong emission peaks are narrow bands at 598 nm, 602 nm, 619 nm, 651 nm, and 735 nm. Among them, the Pr$^{3+}$ doping concentration has a great influence on the peak shape of the emission peak: when the Pr$^{3+}$ molar doping concentration is low (0.1%), the strongest emission peak of Li$_2$CaSiO$_4$:Pr$^{3+}$
phosphor is located at 598nm; When the molar doping concentration of Pr$^{3+}$ is high (>0.1%), the strongest emission peak of Li$_2$CaSiO$_4$:Pr$^{3+}$ phosphor is located at 619nm. And the calculation found that the color coordinates corresponding to the two typical Pr$^{3+}$ molar doping concentrations (0.001, 0.01) are in the orange light region. This shows that Li$_2$CaSiO$_4$:Pr$^{3+}$ phosphor is a potential orange phosphor that can be used for white LED lighting.

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