Effect of charge compensation on emission spectrum of Ca_2SiO_4:Dy^{3+} phosphor

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The Ca_2SiO_4:Dy^{3+} phosphor was synthesized by the high temperature solid-state reaction method in air. The emission spectrum of Ca_2SiO_4:Dy^{3+} phosphor shows several bands at 486, 575, and 665 nm under the 365-nm excitation. The effects of Li^+, Na^+, and K^+ on the emission spectrum of Ca_2SiO_4:Dy^{3+} phosphor were studied. The results show that the emission spectrum intensity is greatly influenced by Li^+, Na^+, and K^+. The charge compensation concentration corresponding to the maximum emission intensity is different with different charge compensations.

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Recently, the optical conversion materials have been investigated extensively due to their widely applications, such as white light emitting diodes (LEDs) and optical storage[1−3]. The emission spectrum intensity of these materials is an important index which can scale the capability of the materials. Some research results were already reported in this region, for example, the emission spectrum intensity was enhanced by sensitivity of Ce^{3+} or Bi^{3+} to Dy^{3+} in borate phosphor[4−6], and by doping Li^+ in $SrTiO_3$:Pr^{3+} and Y_2O_3:Eu phosphors[7,8]. However, the research on the emission spectrum intensity enhanced by doping charge compensation Li^+, Na^+ and K^+ in silicate phosphor has not been put up. So, in our research, the emission spectrum intensity of doping Li^+, Na^+ and K^+ in Ca_2SiO_4:Dy^{3+} is studied, and the results can help the development of optical conversion materials.

The phosphor was synthesized by high temperature solid-state reaction method in air. $CaCO_3$ (99.9%), SiO_2 (99.9%), Dy_2O_3 (99.99%), Li_2CO_3 (99.9%), Na_2CO_3 (99.9%), and K_2CO_3 (99.9%) were used as starting materials. The mol ratio of $CaCO_3$ to SiO_2 was 2:1 in this experiment. After all the individual materials were sufficiently mixed, the mixed materials were calcined at 1300 °C for 6 h, then Ca_2SiO_4:Dy^{3+} was obtained. The excitation spectrum was measured by a SHIMADZU RF-540 ultraviolet spectrophotometer. The emission spectrum was measured by a SPEX1404 spectrophotometer. All the luminescence characteristics of the phosphors were investigated at room temperature.

The emission and excitation spectra of Ca_2SiO_4:Dy^{3+} phosphor are shown in Fig. 1, and the Dy^{3+} concentration is 2 mol.-%. The emission spectrum exhibits several bands at 486, 575, and 665 nm corresponding to the electric dipole $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition of Dy^{3+}, respectively, and the excitation wavelength is 365 nm. The excitation spectrum for 575 nm indicates that the phosphor can be effectively excited by ultraviolet (331, 361, 371, and 397 nm) and blue (435, 461, and 478 nm) light, and some excitation peaks originate from the $^6H_{15/2} \rightarrow {}^4D_{7/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^6M_{21/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^6F_{9/2}$ of transitions of Dy^{3+}, respectively. The results mean two hands. On the one hand, Ca_2SiO_4:Dy^{3+} phosphor can be effectively excited by 464-nm blue light, and emit 575-nm yellow light, the two emission bands combine to produce a spectrum that appears white to the naked eye; moreover, the "White" light has a good coloration because of the existing of the 665-nm red emission. On the other hand, Ca_2SiO_4:Dy^{3+} phosphor can be effectively excited by ultraviolet light, and emit blue, yellow and red light; the three emission bands can also give a white light. So, Ca_2SiO_4:Dy^{3+} is a promising phosphor for white LEDs.

When trivalent metallic ions, such as Dy^{3+}, are incorporated into a host lattice and substitute for divalent metallic ions, the charge balancing is necessarily required. For Ca_2SiO_4:Dy^{3+}, the incorporation of alkali metal ions can neutralize the charge generated by Dy^{3+} substitution for Ca^{2+}, and thus stabilize the structure and enhance the luminescence. Figures 2 − 4 show the emission spectrum of Li^+, Na^+ and K^+ doping Ca_2SiO_4:Dy^{3+} phosphor, respectively. Li^+, Na^+ and K^+ concentration are all from 1 mol.-% to 6 mol.-%, and the Dy^{3+} concentration is 2 mol.-% in this research. The results show that the evolvement trend is the same with different

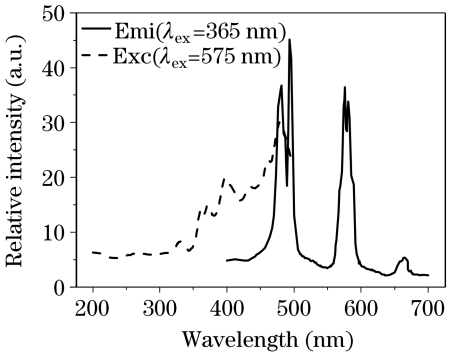

Fig. 1. Excitation and emission spectra of Ca_2SiO_4:Dy^{3+} phosphor.

charge compensations, i.e., the emission spectrum intensity firstly increases with the increase of the charge compensation concentration, then decreases. However, the charge compensation concentration corresponding to the maximal emission intensity is different with different charge compensations, and the concentration is 4 mol.-%, 4 mol.-%, and 3 mol.-% corresponding to Li^+, Na^+, and K^+, respectively. And the maximal emission intensity of doping Li^+ is higher than that of doping Na^+ and K^+, the result is in well agreement with Ref. [9].

The above results can be explained by the following reasons. When the charge compensation is incorporated into a host lattice, the aberration is brought in the crystal lattice, which induces the probability of transition emission and enhances the emission spectrum intensity of Ca_2SiO_4:Dy^{3+} phosphor. However, the emission spectrum intensity of Ca_2SiO_4:Dy^{3+} does not increase all along with the increase of the charge compensation concentration. This means that only portion charge compensation is incorporated into a host lattice, when the doping concentration is higher than the Dy^{3+} concentration, the excrescent part will substitute for the Ca^{2+} site, and the excrescent negative charge will engender, which makes the emission spectrum intensity decrease[7].

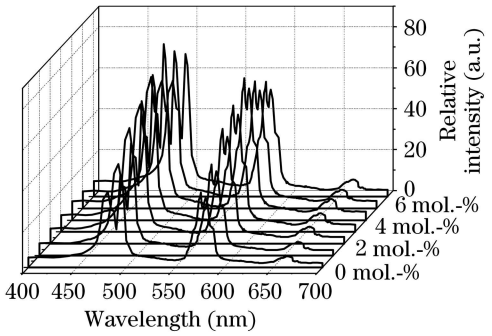

Fig. 2. Emission spectrum intensity of Ca_2SiO_4:Dy^{3+} phosphor as a function of Li^+ concentration.

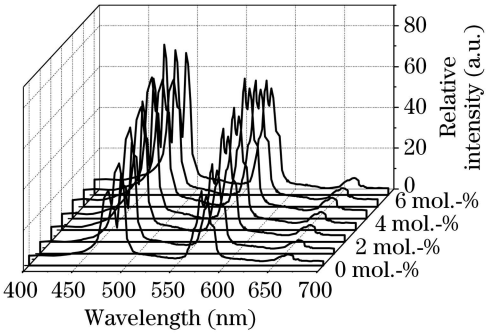

Fig. 3. Emission spectrum intensity of Ca_2SiO_4:Dy^{3+} phosphor as a function of Na^+ concentration.

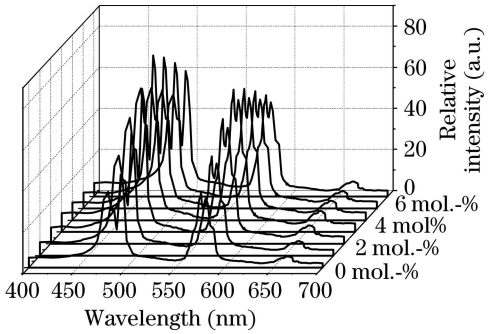

Fig. 4. Emission spectrum intensity of Ca_2SiO_4:Dy^{3+} phosphor as a function of K^+ concentration.

The difference of charge radii can explain that the charge compensation concentration corresponding to the maximum emission intensity is different with different charges. The radius of Ca^{2+} in the host lattice is 0.112 nm, and the radii of Li^+, Na^+, and K^+ are 0.059, 0.116, and 0.133 nm, respectively. Comparing with K^+ ion, Li^+ and Na^+ are easy incorporated into the host lattice, so the doping concentration is higher than K^+, and the doping concentration is 4 mol.-% and 4 mol.-%, respectively.

In conclusion, the Ca_2SiO_4:Dy^{3+} phosphor was synthesized by the high temperature solid-state reaction method in air. The emission spectrum of Ca_2SiO_4:Dy^{3+} phosphor shows several bands at 486, 575, and 665 nm under the 365-nm excitation. The emission spectrum intensity of Ca_2SiO_4:Dy^{3+} phosphor firstly increases with the increase of the charge compensation concentration, then decreases. The charge compensation concentration corresponding to the maximal emission intensity is different with different charge compensations, and the concentration is 4 mol.-%, 4 mol.-%, and 3 mol.-% corresponding to Li^+, Na^+, and K^+, respectively.

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