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Preparation and luminescence characteristics of Eu^{2+} activated silicate phosphor*

Li Pan-Lai(李盼来)†, Yang Zhi-Ping(杨志平),
Wang Zhi-Jun(王志军), and Guo Qing-Lin(郭庆林)

College of Physics Science & Technology, Hebei University, Baoding 071002, *China*

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This paper synthesizes the $Sr_2SiO_4:Eu^{2+}$ phosphor by high temperature solid-state reaction. The emission spectrum of $Sr_2SiO_4:Eu^{2+}$ shows two bands centred at 480 and 547 nm, which agree well with the calculation values of emission spectrum, and the location of yellow emission of $Sr_2SiO_4:Eu^{2+}$ is influenced by the Eu^{2+} concentration. The excitation spectrum for 547 nm emission has two bands at 363 and 402 nm. The emission spectrum of white light emitting diodes (w-LEDs) based on $Sr_2SiO_4:Eu^{2+}$ phosphor + InGaN LED was investigated.

Keywords: white LED, $Sr_2SiO_4:Eu^{2+}$, luminescence characteristics
PACC: 7855

1. Introduction

Recently, the white light emitting diodes (w-LEDs) have been investigated extensively due to their application, such as back-lighting for liquid crystal displays and daily-lighting-lamps.[1−4] The w-LED can be fabricated by three ways,[5] i.e., the light transition model, the multicolour combination model and the quantum well model. At present, the light transition model has been achieved commercially, e.g., the w-LED based $YAG:Ce^{3+}$ + InGaN LED.[6] With the development of the w-LED, the blue LED + yellow phosphor has become the main model. However, very few novel yellow phosphors with high efficiency were actually discovered, except for the YAG:Ce phosphor and some organic luminescent materials. So, we attempted to develop a yellow phosphor that emits efficiently under the blue light excitation. In this research, $Sr_2SiO_4:Eu^{2+}$ phosphor was synthesized by the high temperature solid-state reaction and its luminescence characteristics were investigated.

2. Experimental details

The phosphor was synthesized by the general high temperature solid-state reaction. The starting materials $SrCO_3$, SiO_2 and Eu_2O_3 were all with purity of 99.9%. After mixed sufficiently, the powder was heated at 1300°C for 6 h under the ambience of 5% H_2 in N_2 to reduce Eu^{3+} to Eu^{2+}. The obtained products were crystalline $Sr_2SiO_4:Eu^{2+}$ emitting yellow luminescence.

The phase present of the samples was characterized by powder x-ray diffraction (XRD) (D/max-rA, Cu Kα, 40 kV, 40 mA, $\lambda = 1.5406$ nm). The excitation spectrum was measured by a SHIMADZU RF-540 ultraviolet spectrophotometer. The emission spectrum was measured by a SPEX1404 spectrophotometer. All the characteristics of the phosphors were conducted at room temperature.

3. Results and discussion

3.1. The structure of $Sr_2SiO_4:Eu^{2+}$ phosphor

The XRD pattern of $Sr_2SiO_4:Eu^{2+}$ phosphor with Eu^{2+} concentration 1 mol% is presented in Fig.1. All patterns agree well with JCPDS file 39-1256, indicating that the doped Eu^{2+} ions have not caused any significant change in the host structure. Sr_2SiO_4 has an orthorhombic crystal structure, and their lattice parameters values are $a = 0.7079$ nm, $b = 0.5672$ nm, $c = 0.9743$ nm.

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†Corresponding author. E-mail: lipanlai@sohu.com

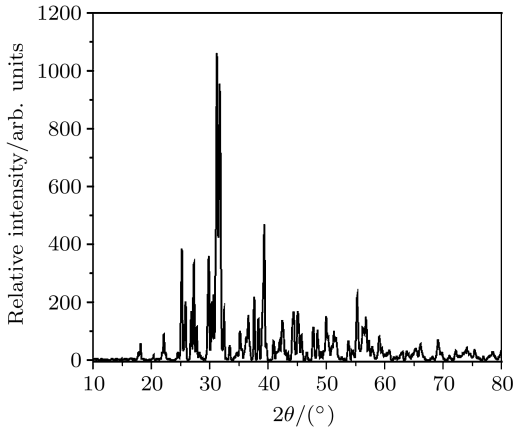


Fig.1. XRD pattern of $Sr_2SiO_4:Eu^{2+}$ phosphor.

3.2. The excitation and emission spectra of $Sr_2SiO_4:Eu^{2+}$ phosphor

The emission and excitation spectra of $Sr_2SiO_4:Eu^{2+}$ phosphor are shown in Fig.2. $Sr_2SiO_4:Eu^{2+}$ shows two emission bands, one is centred at 480 nm, the other is centred at 547 nm. And the excitation spectrum for 547 nm emission has two excitation bands at 363 and 402 nm, respectively. The results indicate that the phosphor used for w-LEDs can be excited by UV and blue light.

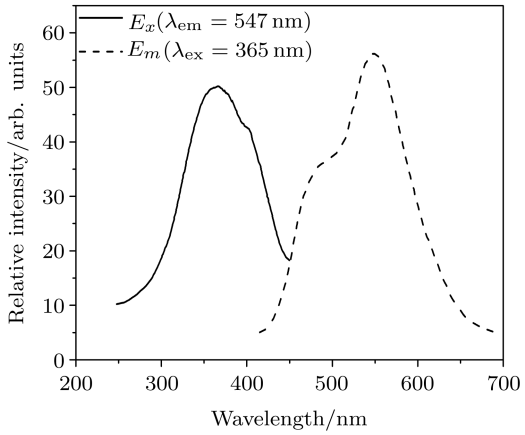


Fig.2. The emission and excitation spectra of $Sr_2SiO_4:Eu^{2+}$ phosphor $\lambda_{em} = 547$ nm; $\lambda_{ex} = 365$ nm.

The experiment showed that the host material Sr_2SiO_4 has no luminescence. However, the two emission peaks are observed for $Sr_2SiO_4:Eu^{2+}$ phosphor, which indicates two sites of Sr^{2+} existed in Sr_2SiO_4 lattice,[7] viz., Sr^{2+}(I) coordinated with eight oxygen atoms and Sr^{2+}(II) coordinated with six oxygen atoms. When Sr^{2+} was replaced by Eu^{2+}, accordingly two types of Eu^{2+}, Eu^{2+}(I) and Eu^{2+}(II), were formed, which led two luminescence centres. Therefore, the emission spectrum exhibits two peaks at 480 and 547 nm, respectively, corresponding to the electric dipole transition 4f5d $\rightarrow {}^1S_{7/2}$ of Eu^{2+}. Since two luminescence centres have different properties, they performed different emission intensities.

Van Uitert[8] had investigated several Eu^{2+} or Ce^{3+}-doped compounds, such as the sulfides, oxides, halides and aluminates. The results show that the energy position for the 5d-band edge of Eu^{2+} or Ce^{3+} in various compounds can be determined by

$$E = Q[1 - (V/4)^{1/V} \times 10^{-(n\cdot e_a\cdot r)/8}](\mathrm{cm})^{-1},$$

where Q is the position of energy of the lower d-band edge for the free ion ($Q = 34000\,\mathrm{cm}^{-1}$ for Eu^{2+}), V is the valence of the active cation ($V = 2$), n is the number of anions in the immediate shell around this ion, e_a is the electron affinity of the atoms that form the anions, and r is the radius of the host cation replaced by the activator cation in the host crystal.

For $Sr_2SiO_4:Eu^{2+}$ phosphor, the value of e_a can be obtained by the lower value of index with various compounds, such as $e_a = 1.17$ eV for simple compound, $e_a = 1.60$ eV for $Y_3Al_5O_{12}$ and $GaAlO_3$, e_a is higher than that for SiO_4^{4-}, PO_4^{3-} and WO_4^{2-}, and increases with increasing the charge of central atom. So e_a is 2.19 eV because the charge of Si atom in SiO_4^{4-} is higher than Al in aluminates.[8,9] In Sr_2SiO_4, r is 0.118 nm for six oxygen coordinated Sr and 0.126 nm for eight oxygen coordinated. The E values of Eu^{2+}(I) and Eu^{2+}(II) were calculated by the above equation and listed in Table 1.

Table1 shows that the experimental values agree well with the calculated values, it can be concluded that the primary emission band centred at 547 nm originates from the Eu^{2+} (II) site, and the weaker emission band centred at 480 nm originates from the Eu^{2+} (I) site.

Table 1. Energy position of d edge for Eu^{2+} in Sr_2SiO_4.

n	e_a/eV	r/nm	E/cm^{-1}	λ_{emi}/nm (Calculation)	λ_{emi}/nm (Experiment)
6	2.19	0.118	18832	537	547
8	2.19	0.126	21277	470	480

3.3. The effect of Eu^{2+} concentration on the yellow emission of $Sr_2SiO_4:Eu^{2+}$ phosphor

The effect of Eu^{2+} concentration on the yellow emission of $Sr_2SiO_4:Eu^{2+}$ phosphor was investigated and the result is shown in Table.2. The red shift of the emission peak occurs distinctly with increasing the Eu^{2+} concentrations, which can be interpreted that the number of two luminescence centres exhibits a significant change with increasing Eu^{2+} concentration, and the probability of Eu^{2+} occupying six compounds becomes bigger, so red shift occurs distinctly. The results mean that we can make the emission wavelength longer than YAG:Ce's through increasing the Eu^{2+} concentration, This may enhance the colour development of w-LEDs.

Table 2. Correlation between the peak position of the main emission of $Sr_2SiO_4:Eu^{2+}$ and the Eu^{2+} concentration.

Eu^{2+} concentration/mol%	0.25	0.5	1	3	5
peak wavelength/nm	517	530	547	553	558

3.4. The emission spectrum of the InGaN-based $Sr_2SiO_4:Eu^{2+}$

The emission spectrum of the InGaN-based $Sr_2SiO_4:Eu^{2+}$ is shown in Fig.3. The w-LED based on InGaN + $Sr_2SiO_4:Eu^{2+}$ shows two bands at 400 and 547 nm. The 400 nm emission band is due to a radiative recombination from an InGaN active layer. This emission is used to excite $Sr_2SiO_4:Eu^{2+}$ phosphor. The 547 nm emission band is ascribed to a radiative recombination of Eu^{2+} activators in the Sr_2SiO_4 host. The two emission bands combine to give a spectrum that appears white to the naked eye, so $Sr_2SiO_4:Eu^{2+}$ is a promising yellow phosphor for w-LEDs.

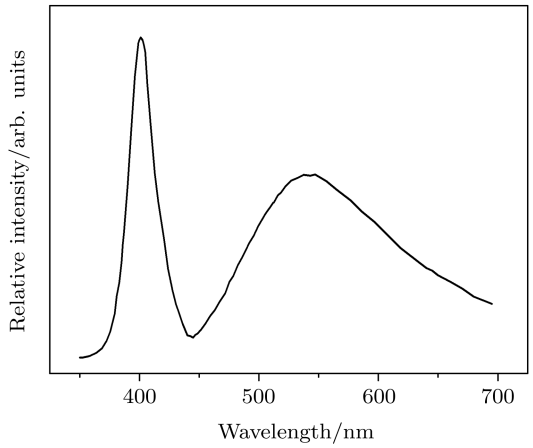


Fig.3. Emission spectrum of InGaN+$Sr_2SiO_4:Eu^{2+}$.

4. Conclusions

In conclusions, $Sr_2SiO_4:Eu^{2+}$ phosphor was synthesized by high temperature solid-state reaction. The emission spectrum of $Sr_2SiO_4:Eu^{2+}$ shows two bands centred at 480 and 547 nm, which agree well with the calculated values of emission spectrum, and the red shift of the yellow emission peak occurs distinctly with increasing the Eu^{2+} concentration. The excitation spectrum for 547 nm emission has two bands at 363 and 402 nm. The emission spectrum of the w-LED based on InGaN+$Sr_2SiO_4:Eu^{2+}$ was investigated, and the result shows that $Sr_2SiO_4:Eu^{2+}$ is a promising yellow phosphor for w-LEDs.

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