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$Ca_9Al(PO_4)_7:Eu^{2+}$的发光、浓度猝灭及温度稳定性

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摘 要:采用高温固相法制备了 $Ca_9Al(PO_4)_7:Eu^{2+}$ 蓝色荧光粉,研究了 $Ca_9Al(PO_4)_7:Eu^{2+}$ 的发光、浓度猝灭及温度稳定性. $Ca_9Al(PO_4)_7:Eu^{2+}$ 的激发光谱覆盖 200~350 nm 紫外区;发射光谱为一主峰位于 445 nm 的宽谱,对应 Eu^{2+} 的 $4f^65d^1\rightarrow4f^7$ 特征跃迁.研究发现,随 Eu^{2+} 掺杂量的增大,$Ca_9Al(PO_4)_7:Eu^{2+}$ 的发射强度呈现先增大、后减小的变化趋势,最大发射强度对应的 Eu^{2+} 掺杂量为 0.01,即存在浓度猝灭效应,对应的机理为电偶极-电偶极相互作用;依据晶格常数,得出临界距离为 2.297 nm. 在 25~300 ℃范围内改变光谱测量温度,发现温度升高到 150 ℃时,$Ca_9Al(PO_4)_7:Eu^{2+}$ 的发射强度变为25 ℃时的 81.0%,对应的激活能为 0.268 eV,说明材料具有较好的温度稳定性.

关键词:发光;浓度猝灭;温度稳定性;Eu^{2+};$Ca_9Al(PO_4)_7$
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Luminescence, Concentration Quenching and Thermal Stability of $Ca_9Al(PO_4)_7:Eu^{2+}$

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Abstract: $Ca_9Al(PO_4)_7:Eu^{2+}$ blue emitting phosphor was synthesized by high temperature solid state method. Luminescence, concentration quenching and thermal stability of $Ca_9Al(PO_4)_7:Eu^{2+}$ were investigated. Excitation spectrum of $Ca_9Al(PO_4)_7:Eu^{2+}$ extended from 200 nm to 350 nm. Under an ultraviolet excitation, $Ca_9Al(PO_4)_7:Eu^{2+}$ showed a broad emission band with a maximum at 445 nm, which corresponded to $4f^65d^1\rightarrow4f^7$ transition of Eu^{2+}. Emission intensities of $Ca_9Al(PO_4)_7:Eu^{2+}$ were influenced by Eu^{2+} concentration, and they enhanced with increasing Eu^{2+} concentration, and reached a maximum value at 0.01 Eu^{2+}, then decreased with further increasing Eu^{2+} concentration because of concentration quenching effect. The concentration quenching mechanism was verified to be dipole-dipole interaction. According to crystal structure data, critical distance can be obtained to be 2.297 nm. The emission intensity of $Ca_9Al(PO_4)_7:Eu^{2+}$ as a function of temperature was explored. When temperature turned up to 150 ℃, the emission intensity of $Ca_9Al(PO_4)_7:Eu^{2+}$ was 81.0% of the initial value at 25 ℃, and the corresponding activation energy was calculated to be 0.268 eV, which could prove the thermal stability of $Ca_9Al(PO_4)_7:Eu^{2+}$.

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0 Introduction

Recently, rare-earths doped phosphors have application to several aspects, such as Light Emitting Diodes (LEDs), Plasma Display Panels (PDPs) and Field Emission Displays (FEDs), and so on[1-3]. As is well known, Eu^{2+} ion is of great interest for application because its d-f emission is partly- allowed, resulting in high emission intensity[4]. Emission energy shows strong dependence on crystal field and covalence, and Eu^{2+} doped samples usually have strong absorption in the region of Ultraviolet (UV)- visible spectra, and exhibit broad emission band covering color from blue to red region[5]. Especially, host compound has several crystallographic sites, which can serve as a host for several center luminescence materials when Eu^{2+} ions are doped into the compound, and lead to different emission color of Eu^{2+} ion in single compound[6]. Generally, phosphors consist of activator and host, in order to achieve efficient emission phosphor, the host is another key factor. A large number of phosphate compounds have a wide emission distributing under UV to visible light irradiation, therefore, they are regarded as a kind of promising optoelectronic materials[7-10]. For the phosphates, the structure $M_9Ln(PO_4)_7$ (M = Ca, Sr and Ba; Ln = Y and Al, etc.) has attracted extensive attention as host materials for lanthanide activators[11-15]. However, to the best of our knowledge, there is few systematical reports about the luminescence of Eu^{2+} in $Ca_9Al(PO_4)_7$. Therefore, in the present work, $Ca_9Al(PO_4)_7:Eu^{2+}$ is synthesized by solid state method, and luminescence, concentration quenching and thermal stability of $Ca_9Al(PO_4)_7:Eu^{2+}$ are investigated.

1 Experimental

1.1 Sample preparation

$Ca_{9(1-x)}Al(PO_4)_7:xEu^{2+}$ (x: molar concentration) samples are synthesized by a high temperature solid-state method. The initial materials $CaCO_3$ (A. R.), Al_2O_3 (A. R.), $NH_4H_2PO_4$ (A. R.) and Eu_2O_3 (99.99%), are weighed in stoichiometric proportion, thoroughly mixed and ground by an agate mortar and pestle for more than 30 min till they are uniformly distributed. The obtained mixtures are heated at 1 200 ℃ for 10 h in crucibles along with a reducing atmosphere (5% H_2/95% N_2), and then are naturally cooled to room temperature. In order to measure the characteristics of phosphor, the samples are grind into powder.

1.2 Materials characterization

The phase formation is determined by X-ray Diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu $K\alpha1$ radiation (λ=0.154 06 nm), and a scan rate of 0.02°/s is applied to record the patterns in the 2θ range from 10° to 60°. The steady time resolved photoluminescence spectra, the excitation and emission spectra are detected by a fluorescence spectrophotometer (Hitachi F-4600), and the exciting source is a 450 W Xe lamp. All measurements are carried out at room temperature.

High-temperature photoluminescence spectra are detected by the Hitachi F-4600 with a TAP-02 high temperature control system, scanning wavelength range from 400 to 700 nm, spectral resolution of 0.2 nm, and exciting source is a 450 W Xe lamp.

2 Results and discussion

2.1 Phase formation

Fig. 1 presents the XRD patterns of $Ca_9Al(PO_4)_7:xEu^{2+}$ (x = 0.001-0.03). It is obvious seen that the diffraction peaks of all the samples can be exactly assigned to the pure phase of $Ca_9Al(PO_4)_7$ according to JCPDS # 48-1192. The uniform diffraction pattern means that phase formation of $Ca_9Al(PO_4)_7$ is not influenced by a little amounts of Eu^{2+}. $Ca_9Al(PO_4)_7$ has a β-$Ca_3(PO_4)_2$ structure with a space group R3c (161), and the volume of unit cell V=3.426 6 nm^3.

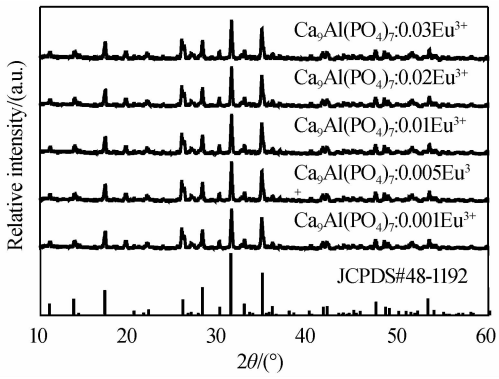

Fig. 1 XRD pattern of $Ca_9Al(PO_4)_7:xEu^{2+}$ (x = 0.001—0.03) with the standard data of $Ca_9Al(PO_4)_7$ (JCPDS No. 48-1192)

2.2 Luminescence and concentration quenching of $Ca_9Al(PO_4)_7:Eu^{2+}$

Fig. 2 depicts the emission spectra of $Ca_9Al(PO_4)_7:xEu^{2+}$ (x = 0.001-0.05). The results show that the positions of emission bands have no obvious change for all the phosphors. They exhibit blue emission band at 445 nm, which corresponds to the f-d

transition of Eu^{2+}. The broad luminescence of Eu^{2+} is due to the $4f^65d^1$ ($4f^7$ transition, which is an allowed electrostatic dipole transition. However, the emission intensities of $Ca_9Al(PO_4)_7:xEu^{2+}$ are obviously influenced by Eu^{2+} concentration. At first, the emission intensities enhance with increasing Eu^{2+} content (x), and achieve a maximum at $x=0.01$, then decrease with further increasing its content because of concentration quenching effect, thus the optimum content is $x=0.01$. For $Ca_9Al(PO_4)_7:xEu^{2+}$ ($x=0.001$-0.05), the excitation spectra have the similar spectral distribution, as a representative, inset of Fig. 2 shows the excitation spectrum of $Ca_9Al(PO_4)_7:0.01Eu^{2+}$, there is a broad band from 200 to 350 nm, and the peak locates at 305 nm which is assigned to $4f^7\rightarrow4f^65d^1$ transition of Eu^{2+} ion.

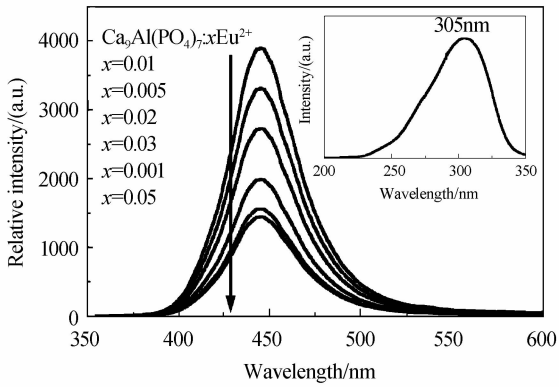

Fig. 2 Emission spectra of $Ca_9Al(PO_4)_7:xEu^{2+}$ ($x=0.001$-0.05) ($\lambda_{ex}=305$ nm), and excitation spectrum of $Ca_9Al(PO_4)_7:0.01Eu^{2+}$ ($\lambda_{em}=445$ nm)

In the previous work[16], the concentration quenching mechanism is cursorily explored, and is dipole-dipole interaction by Dexter theory. However, if using the Dexter theory, some conditions must be considered, therefore, the concentration quenching mechanism of $Ca_9Al(PO_4)_7:Eu^{2+}$ should be anew discussed. According to Blasse[17], if activator is introduced solely on Z (for $Ca_9Al(PO_4)_7$, Z=Ca) ion sites, x_c is the critical concentration. N is the number of Z ions in the unit cell and V is the volume of the unit cell, the critical distance (R_c) of energy transfer can be calculated by using the concentration quenching method, and estimated by the following formula[17]

$$R_c\approx2[3V/(4(x_cN)]^{1/3} \quad (1)$$

where x_c is the concentration of Eu^{2+}, i. e. $x_c=9x$ for $Ca_9Al(PO_4)_7:xEu^{2+}$. N is the number of Z ions in the unit cell (for $Ca_9Al(PO_4)_7$, $N=6$), and V is the volume of unit cell (for $Ca_9Al(PO_4)_7$, $V=3.426\ 6\ nm^3$). The estimated distance (R_c) for $Ca_9Al(PO_4)_7:xEu^{2+}$ phosphors ($x_c=0.009$, 0.045, 0.09, 0.18 and 0.27) are 4.950, 2.895, 2.297, 1.823 and 1.593 nm, respectively. The distances become shorter with increasing Eu^{2+} content. Therefore, the concentration quenching mechanism of Eu^{2+} in $Ca_9Al(PO_4)_7$ can be approximately calculated by Eq (1). By taking the appropriate values of V, N and x_c (3.426 6 nm^3, 6, 0.09, respectively), the critical distance (R_c) of Eu^{2+} in $Ca_9Al(PO_4)_7$ is found to be 2.297 nm.

Non-radiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion may occur by exchange interaction, radiation reabsorption or multiple-multiple interaction. Eu^{2+} is an isolated emission center in $Ca_9Al(PO_4)_7:Eu^{2+}$. The $4f^7$ ($4f^65d^1$ transition of Eu^{2+} is allowed while exchange interaction is responsible for the energy for forbidden transitions and typical critical distances are then about 0.5 nm[18]. It means that the mechanism of exchange interaction plays no role in energy between Eu^{2+} ions in $Ca_9Al(PO_4)_7:Eu^{2+}$. The mechanism of radiation reabsorption comes into effect only when there is broad overlap of the fluorescent spectra of sensitizer and activator, and in the view of the emission and excitation spectra of $Ca_9Al(PO_4)_7:Eu^{2+}$ is unlikely to be occurring in the case. The concentration quenching mechanism of Eu^{2+} in $Ca_9Al(PO_4)_7:Eu^{2+}$ may be the electric multiple-multiple interaction by Dexter's theory. If the energy transfer occurs between the same sorts of activators, the multipolar interaction can be determined from the change of the emission intensity. The emission intensity per activator ion follows the equation[19]

$$(I/x)=K[1+\beta(x)^{Q/3}]^{-1} \quad (2)$$

where x is the activator concentration; $Q=6$, 8, 10 for dipole-dipole (d-d), dipole-quadrupole (d-p), quadrupole-quadrupole (q-q) interactions, respectively; K and β are constant for the same excitation conditions for a given host crystal.

Fig. 3 shows the emission intensity of Eu^{2+} in $Ca_9Al(PO_4)_7$ under 305 nm excitation, and it reaches a maximum value at $x=0.01$. Fig. 3 depicts the plot of $\log I/x_{Eu}^{2+}$ as a function of $\log x_{Eu}^{2+}$ in $Ca_9Al(PO_4)_7:Eu^{2+}$. The dependence of $\log I/x_{Eu}^{2+}$ on $\log x_{Eu}^{2+}$ is linear and the slope is -1.85, and the value of Q can be calculated as

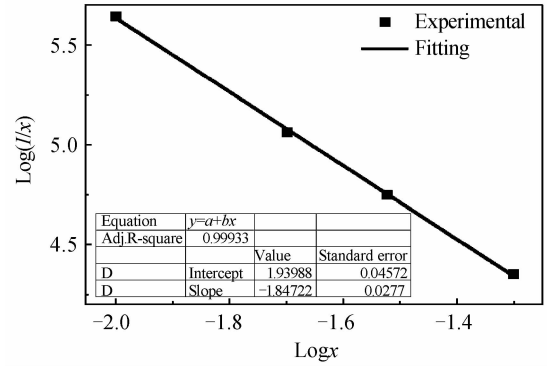

Fig. 3 Plot of $\log(I/xEu^{2+})$ as a function of $\log xEu^{2+}$ in $Ca_9Al(PO_4)_7:xEu^{2+}$ ($\lambda_{ex}=305$ nm)

5.55, and approximately equal to 6. It means that the concentration quenching mechanism of Eu^{2+} in $Ca_9Al(PO_4)_7$ is the d-d interaction.

2.3 Thermal stability of $Ca_9Al(PO_4)_7:Eu^{2+}$

For application, the thermal stability of phosphor is one of important issues to be considered. For $Ca_9Al(PO_4)_7:0.01Eu^{2+}$, the temperature dependence of emission intensity under 305 nm excitation is shown in the inset of Fig. 4. It shows the temperature quenching characteristics of $Ca_9Al(PO_4)_7:0.01Eu^{2+}$ in temperature range from 25 to 250 ℃. The results shows that the intensity of sample drops to about 81.0% when temperature is 150 ℃, in other words, the sample has a good thermal quenching property.

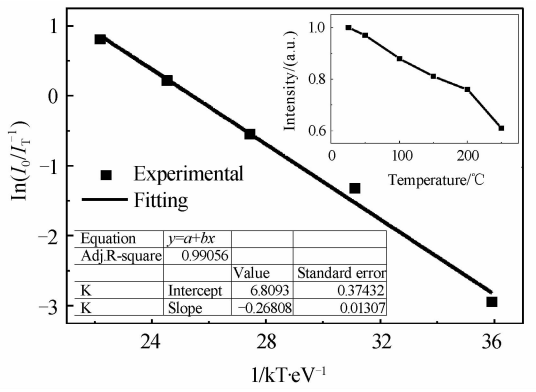

Fig. 4 Arrhenius fitting of emission intensity of $Ca_9Al(PO_4)_7:0.01Eu^{2+}$ and the activation energy (ΔE) for thermal quenching, and emission intensity of $Ca_9Al(PO_4)_7:0.01Eu^{2+}$ as a function of temperature (25～250 ℃)

The activation energy (E_a) can be expressed by[20]

$$\ln(I_0/I)=\ln A-E_a/kT \tag{3}$$

where I_0 and I are luminescence intensity of $Ca_9Al(PO_4)_7:0.01Eu^{2+}$ at room temperature and the testing temperature, respectively. A is a constant, k is the Boltzmann constant (8.617×10^{-5} eV K^{-1}). The fitting result is shown in Fig. 4 and the activation energy ΔE is achieved as 0.268 eV. The relatively high activation energy indicates that $Ca_9Al(PO_4)_7:0.01Eu^{2+}$ has a good thermal stability.

2.4 Chromaticity coordinates $Ca_9Al(PO_4)_7:Eu^{2+}$

Color coordinates are one of the important factors for evaluating performance of phosphor. It is a well known fact that the color coordinates are the same if the spectra profiles are identical. In such case, the color coordinates of $Ca_9Al(PO_4)_7:xEu^{2+}$ ($x=0.001$, 0.005, 0.01, 0.02 and 0.03) are measured, and shown in Table 1. The chromatic standard issued by Commission Internationale de I'Eclairage in 1931 (CIE 1931). It can be seen that the color coordinates of $Ca_9Al(PO_4)_7:xEu^{2+}$ are about the blue region. For example, the CIE color coordinate of $Ca_9Al(PO_4)_7:0.01Eu^{2+}$ is (0.155, 0.057).

Table 1 CIE chromaticity coordinates of $Ca_9Al(PO_4)_7:xEu^{2+}$

Samples	CIE(x, y)
$x=0.001$	(0.156, 0.057)
$x=0.005$	(0.156, 0.058)
$x=0.01$	(0.155, 0.057)
$x=0.02$	(0.156, 0.057)
$x=0.03$	(0.155, 0.056)

3 Conclusions

$Ca_9Al(PO_4)_7:Eu^{2+}$ phosphors have been synthesized by the high temperature solid-state method. $Ca_9Al(PO_4)_7:Eu^{2+}$ shows an asymmetrically single green emission band with a maximum at 445 nm, and for 445 nm emission, the excitation spectrum presents a broad absorption from 200 to 350 nm with a peak at 305 nm. The Eu^{2+} doped concentration not only influences the emission intensities of $Ca_9Al(PO_4)_7:Eu^{2+}$ but also occurs to the concentration quenching effect. The critical distance can be calculated as 2.297 nm. The concentration quenching mechanism of Eu^{2+} in $Ca_9Al(PO_4)_7:Eu^{2+}$ is determined to be d-d interaction. $Ca_9Al(PO_4)_7:Eu^{2+}$ has a good thermal stability, at 150 ℃, emission intensity of $Ca_9Al(PO_4)_7:0.01Eu^{2+}$ is 81.0% of the initial value at room temperature, and activation energy ΔE is calculated to be 0.268 eV.

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