Luminescent properties of blue emitting phosphor SrZn$_2$(PO$_4$)$_2$:Eu^{2+} for white LEDs*

LU Wei (陆伟)[1], **LIU Yu-fei** (刘宇飞)[2], **WANG Ying** (王颖)[3], **WANG Zhi-jun** (王志军)[3]**, and PANG Li-bin** (庞立斌)[3,4]**

1. Tangshan Vocational & Technical College, Tangshan 063000, China

2. Library, Hebei University, Baoding 071002, China

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

4. Department of Foreign Language Teaching and Research, Hebei University, Baoding 071002, China

Blue emitting phosphor SrZn$_2$(PO$_4$)$_2$:Eu^{2+} is synthesized by a high temperature solid state method, and the luminescent properties are investigated. At the 330 nm radiation excitation, SrZn$_2$(PO$_4$)$_2$:Eu^{2+} presents an emission band at 416 nm, which is assigned to the 4f^{6}5d^1→4f^7 transition of Eu^{2+} ion. The concentration quenching effect of Eu^{2+} in SrZn$_2$(PO$_4$)$_2$ has been validated and proved to be a resonant type via a dipole-dipole interaction. The critical distance (R_c) of Eu^{2+} in SrZn$_2$(PO$_4$)$_2$ is calculated to be 3.244 nm. The Commission International de I'Eclairage (CIE) chromaticity coordinates of SrZn$_2$(PO$_4$)$_2$:Eu^{2+} locate at the blue region, such as (0.150, 0.072). The results indicate that the SrZn$_2$(PO$_4$)$_2$:Eu^{2+} phosphor may have potential applications in white light emitting diodes (LEDs).

The traditional method to obtain white light emitting diodes (LEDs) is the combination of a blue LED chip and a yellow phosphor YAG:Ce. However, the white LEDs exhibit a high correlated color temperature ($CCT \approx 7\,750$ K) and a poor color rendering index ($CRI \approx 70$—80), because they are lack of red component[1]. In order to overcome this drawback, white LEDs can be fabricated by combining near ultraviolet (n-UV) or UV LED with red, green and blue phosphors, therefore, it is a research focus to achieve the tri-color phosphors[2]. As well known, for the blue emitting phosphor, Eu^{2+} doped materials are primarily considered because the d-f emission is partly-allowed, resulting in high emission intensity[3]. Especially, the emission energy shows a strong dependence on the crystal field and covalence, and the Eu^{2+} doped phosphors usually have a strong absorption in the region from UV to the visible spectra, and exhibit broad emission band covering the color from blue to red. Therefore, the Eu^{2+} doped phosphors have applications in several aspects[4-6].

Generally, phosphors consist of activator and host. In order to achieve efficient emission, host is the key factor, which must have excellent physical and chemical stability. Among the compounds, phosphate is a good candidate due to its low cost, low synthetic temperature and stability, etc. For example, MZn$_2$(PO$_4$)$_2$ (M=Ca, Sr, Ba) have attracted extensive attention as host compounds for lanthanide activator[7-11]. However, there has no systematic report about the luminescent properties of SrZn$_2$(PO$_4$)$_2$:Eu^{2+}. Therefore, in the present work, the luminescent properties of SrZn$_2$(PO$_4$)$_2$:Eu^{2+} are investigated. The results may be useful for development of blue emitting phosphor.

A series of SrZn$_2$(PO$_4$)$_2$:xEu^{2+} (x is the molar concentration) samples were synthesized by a solid-state method. Initial materials, SrCO$_3$, ZnO, NH$_4$H$_2$PO$_4$ (all materials are of analytical grade) and Eu$_2$O$_3$ (99.99%) were weighed in stoichiometric proportion, thoroughly mixed and ground by an agate mortar and pestle for more than 30 min till they were uniformly distributed. The mixed powders were calcined in corundum crucibles at 900 ºC for 5 h in a reducing atmosphere (5%H$_2$/95%N$_2$). Finally, the samples were cooled down to room temperature and ground thoroughly again into powders.

The phase formation was determined by X-ray diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu Kα1 radiation (λ=0.154 06 nm), and a scan rate of 0.02 °/s was applied to record the patterns in the 2θ range from 10° to 70°. The steady time resolved luminescence

spectra were detected by an FLS920 fluorescence spectrometer, and the exciting sources were a 450 W Xe lamp and an EPL 320-picosecond pulsed diode laser, respectively. Commission International de I'Eclairage (CIE) chromaticity coordinates of phosphors were measured by a PMS-80 spectra analysis system. All measurements were carried out at room temperature.

The compound $SrZn_2(PO_4)_2$ was confirmed to exist as a single phase in the $Sr_3(PO_4)_2$-$Zn_3(PO_4)_2$ system in 1961 by Hummel[12]. Until 1990, the crystal structure of $SrZn_2(PO_4)_2$ was then determined by Hemontoto to be a hurlbutite-type structure with the composition of $CaBe_2(PO_4)_2$[13], and it crystallizes in a monoclinic system with the space group of $P21/c$ (a=0.832 32 nm, b=0.951 01 nm, c=0.903 17 nm and β=92.393°) and has five crystallographically independent cation sites in a unit cell, namely, one seven coordinated Sr^{2+} site, two four-coordinated Zn^{2+} sites, and two four-coordinated P^{5+} sites[13]. Based on the effective ionic radii of cations with different coordination numbers[14], we have proposed that Eu^{2+} ions are expected to occupy the Sr^{2+} and Zn^{2+} sites preferably, since the ionic radius of Eu^{2+} (0.120 nm) is close to that of Sr^{2+} (0.121 nm). However, the P^{5+} sites with ionic radius of 0.017 nm are too small for Eu^{2+} to occupy. In our experiment, similar diffraction patterns of $SrZn_2(PO_4)_2$:$x$$Eu^{2+}$ are observed for each sample. As a representative, the XRD pattern of $SrZn_2(PO_4)_2$:$0.01Eu^{2+}$ is shown in Fig.1(a). When comparing the diffraction data with the standard JCPDS card (No.80-1062) shown in Fig.1(b), the phase formation of $SrZn_2(PO_4)_2$ is not influenced by a little amount of impurity. This means that Eu^{2+} ions are incorporated into the host successfully.

Fig.2 shows $SrZn_2(PO_4)_2$:$0.01Eu^{2+}$ has a broad emission band at 330 nm radiation excitation, and the peak locates at 416 nm which is typically attributed to $4f^65d^1$→$4f^7$ electronic dipole allowed transition of Eu^{2+} ion. Monitored at 416 nm, the excitation spectrum of $SrZn_2(PO_4)_2$:$0.01Eu^{2+}$ depicts two obvious excitation bands, which are mainly due to the transitions of Eu^{2+} from $4f^7$ ground state to $4f^65d^1$ excited state. As shown in Fig.3, a simple model depicts the characteristic emission energy levels of Eu^{2+} in $SrZn_2(PO_4)_2$.
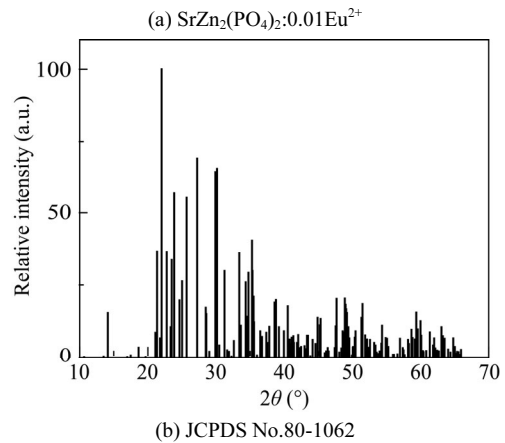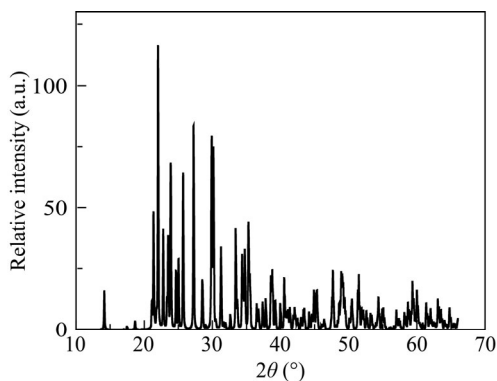

(a) $SrZn_2(PO_4)_2$:$0.01Eu^{2+}$

(b) JCPDS No.80-1062

Fig.1 XRD pattern of $SrZn_2(PO_4)_2$:$0.01Eu^{2+}$ with the standard data of $SrZn_2(PO_4)_2$ (JCPDS No.80-1062)

Fig.2 Emission and excitation spectra of $SrZn_2(PO_4)_2$: $0.01Eu^{2+}$ (λ_{ex}=330 nm, λ_{em}=416 nm) (Inset: Emission intensity of $SrZn_2(PO_4)_2$:$x$$Eu^{2+}$ as a function of Eu^{2+} concentration (λ_{ex}=330 nm))
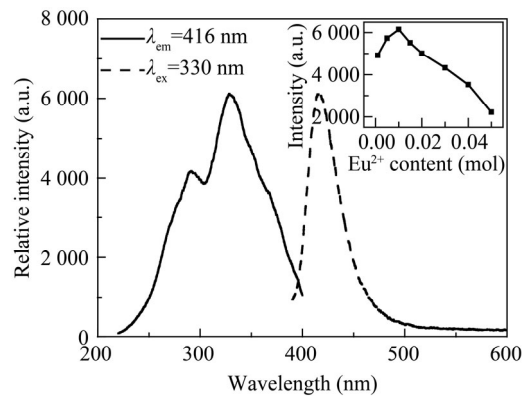
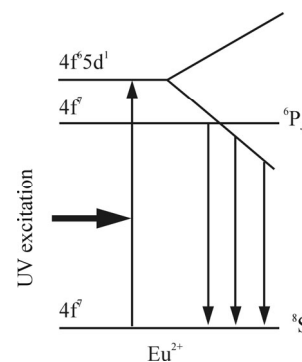**Fig.3 Energy levels of Eu^{2+}**

Inset of Fig.2 presents the emission intensities of $SrZn_2(PO_4)_2$:$x$$Eu^{2+}$ are obviously influenced by Eu^{2+} content, namely, they 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. The increase of emission intensity before

0.01Eu^{2+} could be attributed to the large distance between Eu^{2+} ions, and the reason for decrease is possibly the nonradiative energy transfer between Eu^{2+} ions. Generally, the concentration quenching is mainly caused by the nonradiative energy transfer between Eu^{2+} ions, which usually occurs as a result of an exchange interaction, radiation reabsorption, or a multipole-multipole interaction[15]. It is necessary to obtain the critical distance (R_c) that is the critical separation between the donor (activator) and acceptor (quenching site). According to the report of Blasse[15], if the activator is introduced solely on Z ion sites, where x_c is the critical concentration of the activator ion, N is the number of Z ions in the unit cell, and V is the volume of the unit cell, there is one activator ion per V/x_cN on average. The critical transfer distance (R_c) is approximately equal to twice of the radius of a sphere with this volume
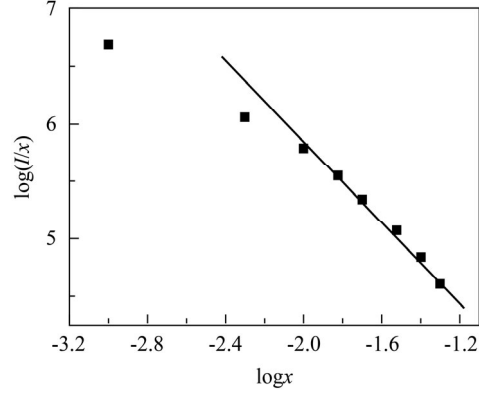
$$R_c \approx 2[3V/(4\pi x_c N)]^{1/3}. \qquad (1)$$

For $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$, x_c is the content of Eu^{2+}, N is the number of Z ions in the unit cell ($N=4$ for $\text{SrZn}_2(\text{PO}_4)_2$), and V is the volume of the unit cell ($V \approx 0.7143\,3\ \text{nm}^3$). In this case, the critical content of Eu^{2+} in $\text{SrZn}_2(\text{PO}_4)_2$ is 0.01. As a result, the R_c value of Eu^{2+} in $\text{SrZn}_2(\text{PO}_4)_2$ is approximately 3.244 nm. When the electric multipolar interaction is involved in the energy transfer, there are several types of interactions, such as dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions. Thus, there is a need to elucidate which type of interaction is involved in the energy transfer. According to the theory of Dexter, the relation between luminescent intensity (I) and the activator content (x) can be expressed by the equation[16]

$$I \propto [(1+A)/\gamma][3\Gamma(1+s/3)/\alpha^{1-s}], \quad (\alpha \geq 1), \qquad (2)$$

where $\alpha = x[(1+A)X_0/\gamma]^{3/s}\Gamma(1-s/3) \propto x$, x is the activator content, s is the series of electric multipolar (for the exchange interaction, d-d, d-q and q-q interactions, the values of s are 3, 6, 8 and 10, respectively), γ is the intrinsic transition probability of activator, A and X_0 are the constants.

From the slope of Eq.(2), the electric multipolar characteristic (s) can be obtained by the slope ($-s/3$) of the plot $\log(I/x)$ versus $\log x$. Fig.4 shows the relation between $\log(I/x)$ and $\log x$ in $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$ ($\lambda_{ex}= 330$ nm). Since the critical content of Eu^{2+} has been determined as 0.01, the dependence of the emission intensity of $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$ excited at 330 nm on the Eu^{2+} content, which is not less than the critical content (0.01), is determined. It can be seen from Fig.4 that the dependence of $\log(I/x)$ on $\log x$ is linear and the slope is -1.669. Thus, the value of s can be calculated as 5.007 (very close to the theoretical value 6 for the electric d-d inter-

action), which means that the d-d interaction is the main mechanism for the concentration quenching of $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$.

Fig.4 Plot of log(I/x) as a function of log$x$ in $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$

To further validate the concentration quenching effect of Eu^{2+} in $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$, we investigate the lifetime of Eu^{2+}. Decay curves of $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$ ($x=0.001-0.05$) excited at 320 nm and monitored at 416 nm are measured. As a representative, Fig.5 shows the decay curve of $\text{SrZn}_2(\text{PO}_4)_2{:}0.01\text{Eu}^{2+}$. For single exponential decay, it can be expressed as[17]

$$I = I_0 \exp(-t/\tau), \qquad (3)$$

where I_0 and I are the intensities at zero time and time t, respectively, and τ is the lifetime for transition. The lifetime for Eu^{2+} is calculated with different Eu^{2+} contents, and the results are shown in the inset of Fig.5. With the lower Eu^{2+} content ($x<0.01$), the lifetime of $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$ becomes only a little shorter with increase of Eu^{2+} content. With further increase of Eu^{2+} content ($x>0.01$), the lifetime of $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$ has an obvious decrease trend. The above results mean that there is the concentration quenching effect of Eu^{2+} in $\text{SrZn}_2(\text{PO}_4)_2{:}x\text{Eu}^{2+}$.
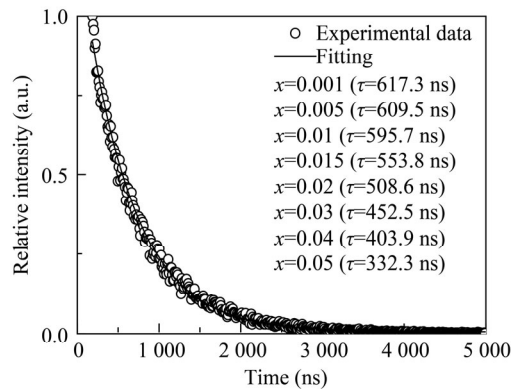
Fig.5 Decay curve of Eu^{2+} in $\text{SrZn}_2(\text{PO}_4)_2{:}0.01\text{Eu}^{2+}$ ($\lambda_{ex}=320$ nm, $\lambda_{em}=416$ nm) (Inset: The decay time of

SrZn$_2$(PO$_4$)$_2$:xEu^{2+} (x=0.001−0.05))

Fig.6 depicts the CIE 1931 chromaticity coordinates of SrZn$_2$(PO$_4$)$_2$:xEu^{2+}. The results show that the CIE chromaticity coordinates of SrZn$_2$(PO$_4$)$_2$:xEu^{2+} locate at blue region, such as SrZn$_2$(PO$_4$)$_2$:0.01Eu^{2+} (0.150, 0.072). The results mean SrZn$_2$(PO$_4$)$_2$:xEu^{2+} may serve as potential blue material for n-UV based white LEDs.
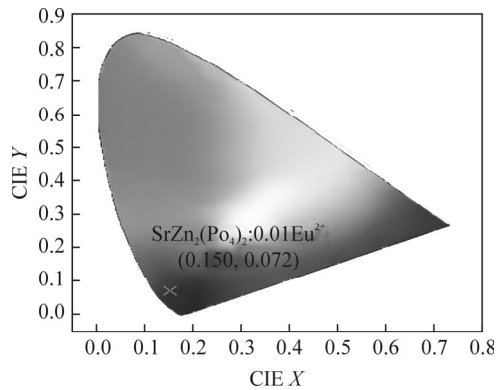
Fig.6 CIE chromaticity coordinates (X, Y) of SrZn$_2$(PO$_4$)$_2$: 0.01Eu^{2+} (λ_{ex}=365 nm)

SrZn$_2$(PO$_4$)$_2$:Eu^{2+} is synthesized by a high temperature solid state method. It can be excited by the 330 nm UV light, and emits blue light, and the 416 nm emission peak is typically attributed to 4f^{6}5d^1→4f^7 electronic dipole allowed transition of Eu^{2+} ion. Its emission intensities can be tuned by changing Eu^{2+} contents, and the optimal content is x=0.01. The mechanism for the concentration quenching of SrZn$_2$(PO$_4$)$_2$:xEu^{2+} is the d-d interaction, and the critical distance (R_c) is about 3.244 nm. The CIE chromaticity coordinates of SrZn$_2$(PO$_4$)$_2$:Eu^{2+} locate at the blue region. The results may be useful for the development of blue emitting phosphors.

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