Improved luminescent properties of SrZn$_2$(PO$_4$)$_2$:Sm$^{3+}$ doped with Li$^+$, Na$^+$ and K$^+$ ions

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$$^*$$^*$$^*

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

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SrZn$_2$(PO$_4$)$_2$:Sm$^{3+}$ phosphor was synthesized by a high temperature solid-state reaction in atmosphere. SrZn$_2$(PO$_4$)$_2$:Sm$^{3+}$ phosphor is efficiently excited by ultraviolet (UV) and blue light, and the emission peaks are assigned to the transitions of $^4$G$_{5/2}$-$^4$H$_{15/2}$ (563 nm), $^4$G$_{5/2}$-$^4$H$_{11/2}$ (597 nm and 605 nm) and $^4$G$_{5/2}$-$^4$H$_{13/2}$ (644 nm and 653 nm). The emission intensities of SrZn$_2$(PO$_4$)$_2$:Sm$^{3+}$ are influenced by Sm$^{3+}$ concentration, and the concentration quenching effect of SrZn$_2$(PO$_4$)$_2$:Sm$^{3+}$ is also observed. When doping A$^+$ ($A$=Li, Na and K) ions, the emission intensity of SrZn$_2$(PO$_4$)$_2$:Sm$^{3+}$ can be obviously enhanced. The Commission Internationale de l’Eclairage (CIE) color coordinates of SrZn$_2$(PO$_4$)$_2$:Sm$^{3+}$ locate in the orange-red region. The results indicate that the phosphor has a potential application in white light emitting diodes (LEDs).

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In recent years, the key of developing white light emitting diodes (LEDs) is the red emitting phosphor that can improve the color rendering index of white LEDs$^1$. Taking account of Sm$^{3+}$ $^4$G$_{5/2}$-$^2$H$_{15/2}$ emission in the red region, it is interesting to develop Sm$^{3+}$ doped samples since such phosphors are expected to possess excellent red color purity$^2$. Nevertheless, the low oscillator strength and narrow line width of Sm$^{3+}$ $^4$F$_{5/2}$-$^4$F$_{7/2}$ absorption transitions will lead to a weak absorption in ultraviolet (UV) region, which leads to that Sm$^{3+}$ doped phosphors present a weak orange-red or red emission. Therefore, it is necessary to find a method to enhance the emission intensity of Sm$^{3+}$ doped phosphors$^3$. Generally, luminescent materials consist of activator and host. In order to obtain efficient emission, the choice of host is another key factor, and the host must have excellent physical and chemical stability$^{4,5}$. Among the compounds, phosphate is a good candidate due to the low cost, low synthetic temperature and good stability. For example, MZn$_2$(PO$_4$)$_2$ ($M$=Ca, Sr and Ba) has attracted extensive attention as host material for lanthanide activators$^6-10$. However, there is no report about the luminescence of SrZn$_2$(PO$_4$)$_2$:Sm$^{3+}$. Hence, in this paper, Sm$^{3+}$ doped SrZn$_2$(PO$_4$)$_2$ was synthesized, and its luminescent properties are improved by using A$^+$ ($A$=Li, Na and K) ions as compensator charge. The results may be useful for the development of red emitting phosphors.

Because of $r_{Sm}$=0.108 nm, $r_{Li}$=0.112 nm and $r_{Na}$=0.074 nm, according to the effective ionic radii of cations with different coordination numbers, Sm$^{3+}$ may preferably occupy Sr$^{2+}$ sites in SrZn$_2$(PO$_4$)$_2$. A series of Sr$_{1-x}$Li$_x$Zn$_2$(PO$_4$)$_2$:xSm$^{3+}$ and Sr$_{1-x}$Zn$_2$(PO$_4$)$_2$:xSm$^{3+}$, xA$^+$ ($A$=Li, Na and K) were synthesized by a high temperature solid-state reaction. Initial materials (analytical grade) of SrCO$_3$, ZnO, NH$_4$H$_2$PO$_4$, Sm$_2$O$_3$, Li$_2$CO$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$ were weighted 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 °C for 5 h in atmosphere. Finally, samples were cooled down to room temperature and ground thoroughly again into powders. Moreover, the samples were sieved under the same condition to ensure the similar particle size distribution.

Phase formation was determined by X-ray diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., Germany) with Ni-filtered Cu Kα1 radiation ($\lambda$=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

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** E-mails: wangzj1998@sohu.com; lizhibin268@sohu.com
70°. Excitation and emission spectra were detected by a fluorescence spectrophotometer (Hitachi F-4600), and the exciting source was a 450 W Xe lamp. Commission International de l’Eclairage (CIE) chromaticity coordinates of phosphors were measured by a PMS-80 spectrophotography system. Each CIE chromaticity coordinate of samples is the average result of three times, and the accuracy is about 0.001. All measurements were carried out at room temperature.

For Sr$_x$Zn$_{2-x}$(PO$_4$)$_2$:A$^+$ and Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:A$^+$ (A=Li, Na and K), a series of similar XRD patterns are observed for each sample. Fig.1 shows the XRD patterns of Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:0.03Sm$^{3+}$, Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:0.03Sm$^{3+}$, 0.03Li$^+$, Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:0.03Na$^+$ and Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:0.03K$^+$. When comparing the diffraction data with the standard JCPDS card (No.80-1062), the results indicate that there is no difference between our samples and Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$. The uniform diffraction pattern means that the phase formation of Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$ is not influenced by a little Sm$^{3+}$ and A$^+$. Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$ monophosphate has monoclinic structure (space group: P2$_1$/c) with $a=0.832\,32$ nm, $b=0.951\,01$ nm, $c=0.903\,17$ nm, $\beta=92.293^{\circ}$ and $z=4$.

![Fig.1 XRD patterns of Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:0.03Sm$^{3+}$ and Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:0.03A$^+$ (A=Li, Na, K), compared with standard data of Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$ (JCPDS No.80-1062)](image)

Fig.2 shows the spectral characteristics of Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:Sm$^{3+}$. For emission peak of 605 nm, the excitation spectrum has a series of peaks. Some peaks at 360 nm, 372 nm, 401 nm and 461 nm are ascribed to the transitions from the ground state to the excited states of Sm$^{3+}$. As shown in Fig.2 and Fig.3(a), among these excitation peaks, the strongest peak located at 401 nm corresponding to the $^5$H$_{5/2} \rightarrow ^7$F$_{5/2}$ transition monitored at 605 nm. Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:Sm$^{3+}$ exhibits several emission peaks, corresponding to the $^4$G$_{5/2} \rightarrow ^6$H$_{5/2}$ (563 nm), $^4$G$_{5/2} \rightarrow ^2$H$_{5/2}$ (597 nm and 605 nm) and $^4$G$_{5/2} \rightarrow ^4$H$_{0/2}$ (644 nm and 653 nm) transitions of Sm$^{3+}$[11]. Among these emission peaks, the red emitting transition is $^4$G$_{5/2} \rightarrow ^4$H$_{1/2}$ (597 nm and 605 nm), which satisfies the selection rule of $\Delta J=\pm 1$, and it indicates that it is an allowed transition as a magnetic dipole (MD) but it is electric dipole (ED) dominated[11]. Therefore, it can be stated that it is partly MD and partly ED natured emission band. The other transition of $^4$G$_{5/2} \rightarrow ^4$H$_{1/2}$ (644 nm and 653 nm) is purely an ED natured emission band, which is sensitive to the crystal field. Generally, the intensity ratio of ED and MD transitions can be used to understand the symmetry of the local environment of the trivalent 4f ions in the investigated host matrix. The larger the intensity of the ED transition, the more the asymmetric nature. In the present work, $^4$G$_{5/2} \rightarrow ^4$H$_{1/2}$ transition of Sm$^{3+}$ ions is measured to be more intense than the MD transition of $^4$G$_{5/2} \rightarrow ^2$H$_{5/2}$, which describes the asymmetric nature of the investigated host.

In order to further optimize the red emission of Sm$^{3+}$, the concentration dependent emission intensity of Sm$_{1-x}$Zn$_{2-x}$PO$_4$:Sm$^{3+}$ ($x=0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.07$ and $0.10$) is studied. The inset of Fig.2 shows that the emission intensity of Sm$_{1-x}$Zn$_{2-x}$PO$_4$:Sm$^{3+}$ enhances with the increase of Sm$^{3+}$ concentration, reaches its maximum value when Sm$^{3+}$ concentration is $0.03$, and then decreases because of the concentration quenching effect. As shown in Fig.3(b), it may be ascribed to the presence of cross-relaxation between Sm$^{3+}$ ions, and this process should be $^4$G$_{5/2} \rightarrow ^4$H$_{1/2} \rightarrow ^4$F$_{9/2}$ for two adjacent Sm$^{3+}$ ions[12].

![Fig.2 Emission and excitation spectra of Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$:0.03Sm$^{3+}$ with $\lambda_{ex}=401$ nm and $\lambda_{em}=605$ nm, respectively (The inset shows the emission intensity of Sr$_{1.2}$Zn$_{0.8}$(PO$_4$)$_2$: xSm$^{3+}$ as a function of Sm$^{3+}$ concentration with $\lambda_{em}=401$ nm.)](image)

![Fig.3 (a) $^4$G$_{5/2} \rightarrow ^4$H$_{1/2}$ ($J=5, 7$ and $9$) transitions of Sm$^{3+}$; (b) Cross-relaxation process](image)

As shown in the inset of Fig.2, the increase of emis-