

A novel long lasting phosphor $\text{Sr}_5(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}:\text{Eu}^{2+},\text{Gd}^{3+}$ prepared in air condition

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Received 23 April 2013; revised 11 July 2013

Abstract: A series of blue long afterglow mixed halide-phosphate phosphors $\text{Sr}_5(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}:\text{Eu}^{2+},\text{Gd}^{3+}$ were synthesized in air by traditional solid-state reaction route. The crystal structures, photoluminescence, thermoluminescence properties and afterglow properties of the phosphors were characterized systematically using X-ray diffraction (XRD), luminescence spectrophotometer, microcomputer thermoluminescence dosimeter and single photon counter, respectively. Under 280 nm excitation, the broadband emissions of Eu^{2+} ions were observed at 445 nm (blue) due to the $4f^7 \rightarrow 4f^65d$ transition. It was demonstrated that there existed the self-reduction of the Eu^{3+} to Eu^{2+} ions in this special halide-phosphate matrix in air condition. The addition of Gd^{3+} ions obviously enhanced the afterglow properties of the single doped Eu^{2+} ions in the halide-phosphate phosphors. And the content of the fluoride anions also had significant influence on the afterglow properties. All results indicated that $\text{Sr}_5(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}:\text{Eu}^{2+},\text{Gd}^{3+}$ might be potential phosphors for long lasting phosphorescence (LLP) materials.

Keywords: $\text{Sr}_5(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}:\text{Eu}^{2+},\text{Gd}^{3+}$; afterglow phosphors; LLP material; self-reduction; rare earths

Since the long lasting phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ with high LLP features was reported by Matsuzawa et al.^[1] in 1996, this new kind of luminescent materials were investigated and studied, and their applications were also broadened from an indicator in dark to the optical storage device. The LLP materials are a kind of energy storage materials that can absorb both ultraviolet (UV) and the visible lights from the sunlight and then gradually release the energy in the darkness at a certain wavelength. Recently, increasing attention has been paid to rare earth ions doped silicate and aluminates matrix phosphors prepared through different methods. For example, the silicates of $\text{Ca}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+},\text{Dy}^{3+}$ ^[2], $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{M}$ ($\text{M}=\text{Dy}^{3+}, \text{La}^{3+}$ or Na^+)^[3] and $\text{Ba}_2\text{ZnSi}_2\text{O}_7:\text{Eu}^{2+},\text{RE}^{3+}$ ($\text{RE}=\text{Dy}, \text{Nd}$)^[4] were reported as potential LLP materials. Aluminates matrix phosphors were also investigated, $\text{MAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$)^[5,6], $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Eu}^{2+},\text{Dy}^{3+}$ ^[7], $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ ^[8], $\text{BaCa}_2\text{Al}_8\text{O}_{15}:\text{Eu}^{2+}$ ^[9] were considered to be excellent LLP materials. All of those phosphors showed excellent LLP property with relatively chemical stability, but the key point was that the synthesis condition of most Eu^{2+} ions doped aluminates and the silicate phosphors needed a reducing atmosphere and a relatively high temperature.

Eu^{2+} ions doped apatite type alkaline-earth halide-phosphates with general formula $\text{M}_5(\text{PO}_4)_3\text{X}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}, \text{X}=\text{F}, \text{Cl}, \text{Br}, \text{OH}$)^[10,11] were known to be promising

as excellent blue emitting phosphors. Though the traditional solid-state reaction can easily synthesize the required materials, it can hardly distinguish Eu^{3+} ions from Eu^{2+} ions in a non-reductive circumstance. That's why we tried to realize the self-reduction of Eu^{3+} ions in this kind of halide phosphate matrix. To the best of our knowledge, the LLP features of the rare earth ions doped halide-phosphate material had rarely been discussed before. In this work, single Eu^{2+} ions activating the mixed crystal structure of $\text{Sr}_5(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}$ phosphors were synthesized by solid-state reaction in air condition. Furthermore, in order to study the LLP property of the rare earth doped halide-phosphate materials, Eu^{2+} ions with other rare earth dopants were co-doped into the matrix, finally, the addition of Gd^{3+} ions obviously enhanced the LLP features. What we must know is that the ratio of F^- ions in the mixed materials also played an important role in the LLP features of the $\text{Eu}^{2+}/\text{Gd}^{3+}$ co-doped alkaline-earth halide-phosphates.

1 Experimental

1.1 Preparation of the samples

$\text{Sr}_{4.99}(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}:\text{Eu}^{2+}_{0.01}$ and $\text{Sr}_{4.98}(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}:\text{Eu}^{2+}_{0.01},\text{Gd}^{3+}_{0.01}$ were prepared by solid state reaction. In a typical process, certain amount of the starting powders, SrCO_3

Foundation item: Project supported by Cooperation Project in Industry, Education and Research of Guangdong Province and Ministry of Education of China (2012B09110044), and the Guangdong Provincial Natural Science Foundation of China (9151009001000052)

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DOI: 10.1016/S1002-0721(12)60386-X

(A.R.), $\text{NH}_4\text{H}_2\text{PO}_4$ (A.R.), NH_4Cl (A.R.), NH_4F (A.R.), Eu_2O_3 (99.99%), Gd_2O_3 (99.99%), were weighed according to the nominal compositions and the NH_4Cl , NH_4F exceeded 10% as for the compensation for the volatilized parts. All these powders would be thoroughly mixed and ground in an agate mortar and pestled for 1 h till they were distributed. Then the ground powders were heated at 900 °C for 2.5 h in air condition. Finally, after all the samples cooled down to the room temperature, the samples would be ground for further characterization. All the samples with the nominal composition and the corresponding numbers were recorded as follows: $\text{Sr}_{4.99}(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}:\text{Eu}_{0.01}^{2+}$ (S1: $x=0$; S2: $x=0.25$; S3: $x=0.5$; S4: $x=0.75$, S5: $x=1$) and $\text{Sr}_{4.98}(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}:\text{Eu}_{0.01}^{2+}, \text{Gd}_{0.01}^{3+}$ (S6: $x=0$; S7: $x=0.25$; S8: $x=0.5$; S9: $x=0.75$, S10: $x=1$).

1.2 Characterization

The phase identification of the phosphor was recorded by the X-ray diffraction using $\text{Cu K}\alpha$ irradiation ($\lambda=0.15406$ nm) at a tube voltage of 36 kV, and a tube current of 20 mA. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured by a fluorescence spectrophotometer (Hitachi F-7000). The delay curves and the TL curves of the samples were recorded through a GSZF-2A single photon counter and an FJ-427A1 microcomputer thermoluminescence dosimeter, respectively.

2 Results and discussion

2.1 XRD of the samples

The XRD patterns of the phosphor are revealed in Fig. 1(a, b). It can be clearly seen that all the patterns sintered at 900 °C were well coincident with the Joint Committee on Powder Diffraction Standards (JCPDS) 83-0974 ($\text{Sr}_5(\text{PO}_4)_3\text{Cl}$) and 17-0609 ($\text{Sr}_5(\text{PO}_4)_3\text{F}$). This indicated that the obtained samples remained a single hexagonal structure after partially replacing Sr^{2+} by Eu^{2+} or $\text{Eu}^{2+}/\text{Gd}^{3+}$ due to the similar radii of the Sr^{2+} (0.112 nm), Eu^{2+} (0.109 nm) and Gd^{3+} (0.0938 nm). And the substitution of F^- for Cl^- also did not have much effect on the XRD pattern. The weak star signals (*) in S1 and S6 stand for the impurity of $\text{Sr}_3(\text{PO}_4)_2$ ^[12] which resulted from the reaction of SrCO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$. The weak impurity of $\text{Sr}_3(\text{PO}_4)_2$ only appeared in $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ matrix might indicate that the compensation of 10% NH_4Cl did not meet the volatilized parts during the high temperature reaction. And 10% excess of NH_4F were considered to be effective as the halogen compensation in the solid-state reaction.

$\text{Sr}_5(\text{PO}_4)_3\text{X}$ ($\text{X}=\text{Cl}, \text{F}$) had a structure with space group $P63/m$ as is shown in Fig. 2, while Sr/Eu pairs of cations were surrounded by the PO_4 tetrahedral anion

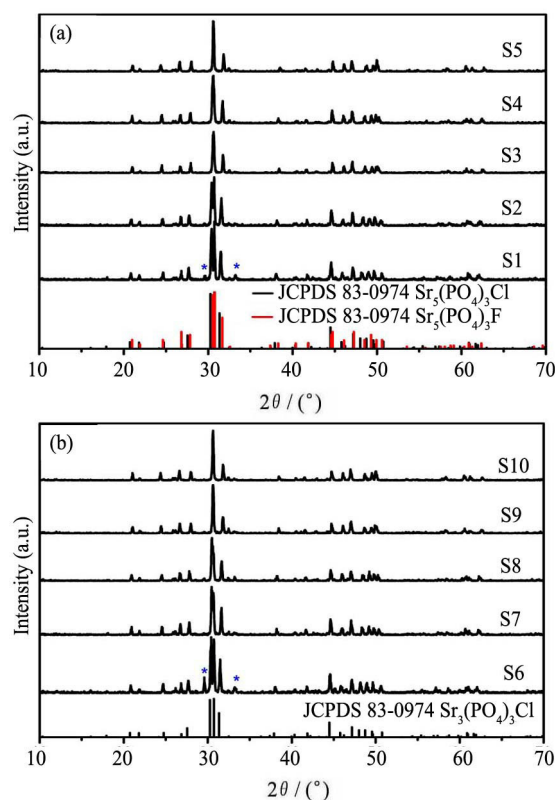


Fig. 1 XRD patterns of the samples (a) S1–S5; (b) S6–S10

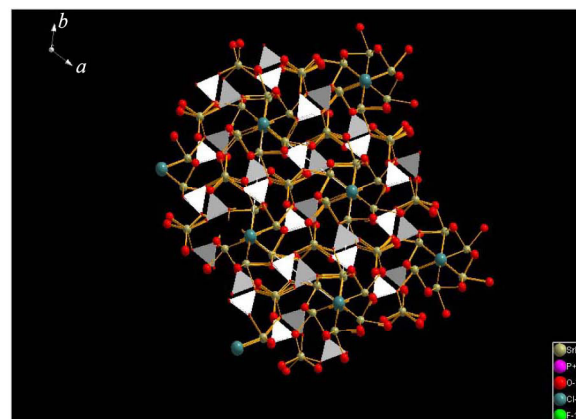


Fig. 2 Projection view of crystal structure of $(\text{Sr,Eu})_5(\text{PO}_4)_3\text{F}_x\text{Cl}_{1-x}$ from the c -axis

groups. Though $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ and $\text{Sr}_5(\text{PO}_4)_3\text{F}$ owned a similar hexagonal crystal structure, they also showed their differences on the cell parameters. The volume of the $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ was 0.60747 nm³, while $\text{Sr}_5(\text{PO}_4)_3\text{F}$ was 0.59575 nm³, and the volume varied as the change of F^- content. The volume values of 0.59733 , 0.60233 and 0.60711 were separately for $x=0.75$, 0.5 and 0.25 . So the introduction of F^- into the $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ would have some effect on the lattice contraction due to the different radii of the Cl^- and F^- .

2.2 PL and PLE of the samples

Fig. 3(a) demonstrates the PL and PLE spectra of the $\text{Sr}_{4.99}(\text{PO}_4)_3(\text{F}_x\text{Cl}_{1-x}):\text{Eu}_{0.01}^{2+}$, and Fig. 3(b) for the

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