The reduction of Eu^{3+} to Eu^{2+} in a new orange–red emission $Sr_3P_4O_{13}$: Eu phosphor prepared in air and its photoluminescence properties

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Abstract

A new orange–red phosphor $Sr_3P_4O_{13}$: Eu was synthesized by a high temperature solid-state reaction. X-ray powder diffraction (XRD) analysis confirms the formation of $Sr_3P_4O_{13}$ in a triclinic system with space group $P\bar{1}$. The photoluminescence spectra indicate that $Sr_3P_4O_{13}$: Eu can be excited effectively by near ultraviolet (NUV) light and exhibit bright orange–red emission with excellent color stability. Interestingly, the emission bands of Eu^{2+} and Eu^{3+} were both observed in the photoluminescence spectra of air-sintered $Sr_3P_4O_{13}$: Eu phosphor due to the self-reduction effect. This kind of abnormal reduction was explained by a charge compensation model.
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1. Introduction

White light-emitting diodes (WLEDs) are known as the new generation lighting source to replace incandescent lamp and fluorescent lamp because of their several advantages such as small size, low energy consumption, long lifetime and environmental protection [1]. The most dominant way to create WLED is by combining a blue chip with yellow phosphor YAG: Ce^{3+} [2]. However, WLED based on this phosphor exhibits a poor color rendering index and a high correlated color temperature due to the lack of red light at long wavelength [3]. In order to improve this problem, another approach to obtain white light was suggested, which is using near ultraviolet (NUV) light InGaN-based LED chip coated with blue/green/red tricolor phosphors [4]. At present, the commercial red-emitting phosphor for NUV InGaN-based WLEDs is still limited to sulfide-based materials such as Y_2O_2S: Eu^{3+} and SrY_2S_4: Eu^{2+}. Sulfide-based phosphors have low efficiency, short working lifetime, and poor chemical stability due to the release of toxic sulfide gas. Therefore,

it is necessary to develop new red phosphors that not only exhibit higher stability but also can be excited effectively by NUV light.

Phosphate materials have been widely investigated because of their excellent thermal and chemical stabilities, low materials cost, important crystallographic possibilities with regard to the accommodation of luminescent ions [5]. Some researchers have reported that phosphate phosphors show stronger emission intensity, higher purity and longer fluorescent lifetime than sulfide phosphors [6,7].

The optical properties of Eu^{3+} doped into matrices are important for the inorganic luminescent materials for its several advantages: (a) the pure red emission of Eu^{3+}, (b) Eu^{3+} is used as a general photo-luminescent probe, (c) the ground state $^7F_0$ and the emitting level $^5D_0$ are non-degenerate and (d) the magnetic dipole $^5D_0$–$^7F_1$ transition is allowed [8].

Inorganic salts containing strontium (Sr) are suitable host materials for Eu^{3+} ions because of the similarity of ionic radii between Sr^{2+} and Eu^{3+}. Especially, Eu^{3+}-doped Sr phosphate have received much attention for the potential applications as new phosphors for WLEDs, such as $SrZn_2(PO_4)_2$: Eu^{3+} [9], $Sr_2P_2O_7$: Eu^{3+} [10], and $LiSrPO_4$: Eu^{3+} [11]. However, to the best of our knowledge, the optical properties of Eu^{3+} ions in $Sr_3P_4O_{13}$ have not been reported.

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In this paper, we report the synthesis and luminescence of a new $Sr_3P_4O_{13}$: Eu phosphor. This phosphor exhibits bright orange–red light emission excited by 394 nm light. At the same time, it is found that the Eu^{3+} ions can be reduced to Eu^{2+} partly in $Sr_3P_4O_{13}$ host in air at a high temperature. The reduction mechanism was discussed in detail.

2. Experiment

The $Sr_3P_4O_{13}$: Eu samples were prepared by a solid state reaction at high temperature with $SrCO_3$ (AR), $NH_4H_2PO_4$ (AR) and Eu_2O_3 (99.99%) as raw materials. The doping concentration of Eu was 4, 8, 12, 16, 20, 24 and 28 mol% in $Sr_3P_4O_{13}$. The stoichiometric amounts of the starting materials were thoroughly mixed, and then heated in an electric furnace at 1000 °C for 6 h. All the preparations were carried out in air atmosphere.

The structures of samples were characterized by an X-ray diffractometer (XRD, D-MAX2500/PC, RIGAKU Corporation of Japan) using 40 kV, 20 mA, and Cu Ka radiation (1.5406 Å). Excitation and emission spectra of the powdered phosphors were measured by a fluorescence spectrometer (F-2700, HITACHI High-Technologies Corporation) and a 450 W xenon lamp was used as the excitation source. All measurements were made at room temperature unless special stated.

3. Result and discussion

3.1. XRD of phosphor powders

Fig. 1 shows the XRD patterns of the $Sr_{3(1-x)}P_4O_{13}$: 3xEu samples synthesized in air. Most of the diffraction peaks of the samples match well with the standard powder diffraction of $Sr_3P_4O_{13}$ (JCPDS card no. 20-1207) confirming the formation of $Sr_3P_4O_{13}$ crystal structure. The compound $Sr_3P_4O_{13}$ crystallizes in a triclinic system and has space group $P\bar{1}$ with unit cell parameters $a=7.2755$ Å, $b=7.7260$ Å, $c=10.1935$ Å and $V=537.75$ Å^3 [12]. However, the intensity of diffraction peaks becomes weaker gradually as the doped Eu concentration increases, suggesting that doping Eu ions would decrease the crystallization of $Sr_3P_4O_{13}$.

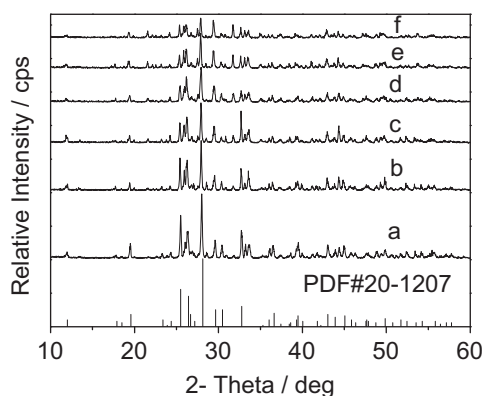### 3.2. Photoluminescence properties of $Sr_3P_4O_{13}$: Eu prepared in air

Fig. 2 exhibits the excitation spectra of $Sr_{2.88}P_4O_{13}$: 0.12Eu synthesized in air atmosphere. Monitored with 427 nm light, the excitation spectrum exhibits a broad excitation band with the maximum peak at 334 nm (shown in Fig. 2a), which can be ascribed to the electron transitions of Eu^{2+} from the ground-state $4f^7$ to the excitation sate $4f^65d^1$ [13]. The excitation band extended from 290 to 400 nm, which nearly covers the whole UV region. However, there are several excitation peaks Fig. 2 when the sample is monitored with 594 nm light (shown in Fig. 2b). The broad excitation band from 220 to 300 nm is attributed to the $O \rightarrow Eu$ charge transitions (CTS), while the sharp lines in the wavelength range of 360–480 nm are due to intra-configurational $4f \rightarrow 4f$ transitions of Eu^{3+} [14]. The $^7F_0 \rightarrow {}^5L_6$ transition at 394 nm is the strongest, which matches the emission spectrum of the NUV InGaN chip.

Fig. 3 shows the emission spectra of $Sr_{2.88}P_4O_{13}$: 0.12Eu excited by 394 nm NUV light. As is known to all, the emission of Eu^{3+} ion generally gives a series of typical line emissions in the spectral region of 570–750 nm corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J=0$–4) transitions, while the emission of Eu^{2+} ion shows a broad band character with a $4f^65d^1 \rightarrow 4f^7$ transition nature. From Fig. 3, it can be seen that the emission spectra consist of two parts. One is the broad band emission around 427 nm, while another is the line emissions in the region of 570–750 nm. The blue band emission located at about 427 nm could be ascribed to $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} [13,15] The line emissions at 588, 594, 613, 654 and 703 nm result from the $^5D_0 \rightarrow {}^7F_J$ ($J=1$, 2, 3, and 4) transitions of Eu^{3+} ions, respectively.

In general, for Eu^{3+} ions, the magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$) can be observed when Eu^{3+} ions occupy the site at center of symmetry, while the electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) will appear when Eu^{3+} ions locate in an asymmetric environment [16]. Zhang reported that all the Sr atoms are coordinated by seven oxygen atoms in $Sr_3P_4O_{13}$, which means that there is only one crystallographic Sr atoms in the structure [12]. However, as shown in Fig. 3, both $^5D_0 \rightarrow {}^7F_1$ transition and $^5D_0 \rightarrow {}^7F_2$ transition are observed in our sample,
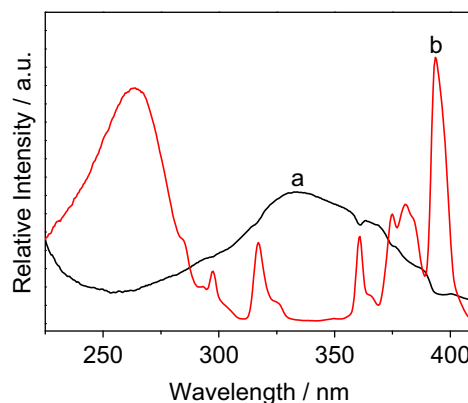

Fig. 1. XRD patterns of $Sr_{3(1-x)}P_4O_{13}$: 3xEu ((a) $x=0.04$, (b) $x=0.08$, (c) $x=0.12$, (d) $x=0.16$, (e) $x=0.20$, and (f) $x=0.24$).

Fig. 2. Excitation spectra of $Sr_{2.88}P_4O_{13}$: 0.12Eu ((a) $\lambda_{em}=594$ nm and (b) $\lambda_{em}=427$ nm).

which imply that there should be two different Eu^{3+} lattice sites. That is to say, there may be two different Sr sites in $Sr_3P_4O_{13}$ lattice, which seems to be contradictory with the crystal structure of $Sr_3P_4O_{13}$ reported by Zhang [12]. This contradictory result was also observed in the emission spectrum of $Sr_3P_4O_{13}$: Eu^{2+} phosphor reported by Zhang et al. [13]. According to reference [13], the emission spectrum of $Sr_3P_4O_{13}$: Eu^{2+} is an asymmetric band at room temperature, while it exhibits two distinct bands when the temperature falls to 20 K. These phenomena also illustrate that there should be two different Sr sites in $Sr_3P_4O_{13}$ lattice, which is consistent with our research results. Detail investigation for the crystal structure of $Sr_3P_4O_{13}$ is still in progress.

The emission spectra of $Sr_3P_4O_{13}$: Eu with different doping concentrations of Eu ions are shown in Fig. 4. The photoluminescence (PL) intensity of Eu^{3+} increases with increasing Eu concentration. The PL intensity at 594 nm increases more

Fig. 3. Emission spectrum of $Sr_{2.88}P_4O_{13}$: 0.12 Eu ($\lambda_{ex}=394$ nm).

Fig. 4. Emission spectra of $Sr_{3(1-x)}P_4O_{13}$: 3xEu ($\lambda_{ex}=394$ nm, $x=0.04$–0.28).

quickly than that at 613 nm. Table 1 shows the ratio of luminescent intensity at 594 and 613 nm. The ratio value increases with the increase of Eu concentration, which also indicates that there are two Sr^{2+} positions in the lattice and centrosymmetric Sr (I) is much easier to be replaced than non-centrosymmetric Sr (II).

3.3. Self-reduction mechanism of Eu^{3+} in $Sr_3P_4O_{13}$: Eu

The emission of Eu^{2+} can also be observed from the emission spectrum of $Sr_3P_4O_{13}$: Eu prepared in air. Su et al. proposed four conditions for the abnormal reduction of $Eu^{3+} \rightarrow Eu^{2+}$ in a solid state compound when prepared in air at a high temperature [17], i.e., (1) no oxidizing ions are present in hosts, (2) the doped Eu^{3+} ion replaces the cations with lower valences in the hosts, (3) the substituted cation has similar radii to Eu^{2+}, and (4) the host compound has appropriate crystal structures, based on tetrahedral anion groups (such as BO_4, PO_4, and AlO_4).

We can consider $Sr_3P_4O_{13}$: Eu based on the four necessary conditions mentioned above. In $Sr_3P_4O_{13}$, Sr^{2+} and P^{5+} are not oxidizing ions, which meet condition (1). The doped Eu^{3+} ions will substitute Sr^{2+} sites and Sr^{2+} has similar radii to Eu^{2+}, which satisfies conditions (2) and (3). Zhang et al. reported that $Sr_3P_4O_{13}$ builds up from SrO_7 polyhedra and $[P_4O_{13}]^{6-}$ polyanions consisting of four PO_4 tetrahedrons [12], which matches condition (4). Therefore, the reduction of Eu^{3+} to Eu^{2+} in $Sr_3P_4O_{13}$: Eu prepared in air is expected to take place. In fact, Eu^{3+} ions have been reduced to Eu^{2+} ions partly.

The reduction of Eu^{3+} to Eu^{2+} in $Sr_3P_4O_{13}$: Eu when prepared in air atmosphere at a high temperature can be explained by charge compensation mechanism [17–19]. When Eu^{3+} ions were doped into $Sr_3P_4O_{13}$, they would substitute the Sr^{2+} ions. To keep electroneutrality of the compound, two Eu^{3+} ions would substitute three Sr^{2+} ions. Therefore, two positive defects of $[Eu_{Sr}]^{*}$ and one negative vacancy defect of $[V_{Sr}]''$ would be created by each substitution for every two Eu^{3+} ions in the compound. Then the vacancy $[V_{Sr}]''$ would act as a donor of electrons while the two $[Eu_{Sr}]^{*}$ defects become acceptors of electrons. By thermal stimulation, electrons of the $[V_{Sr}]''$ vacancies would then transfer to the Eu^{3+} sites and reduce them to Eu^{2+}.

Fig. 5 illustrates the emission spectra of the $Sr_3P_4O_{13}$: Eu samples excited by 334 nm light. The PL intensity of Eu^{2+} decreased with increase of Eu concentration from 4 to 20 mol % until a minimum intensity is reached, and then it was almost unchanged when the doped Eu concentration increased from
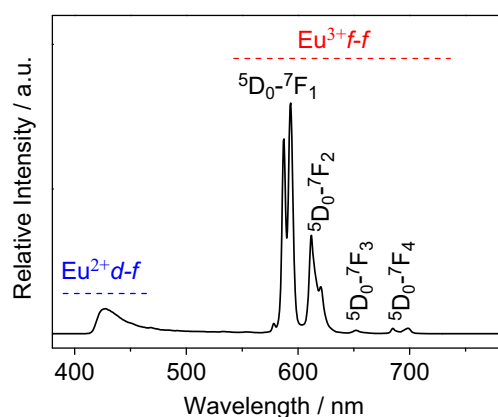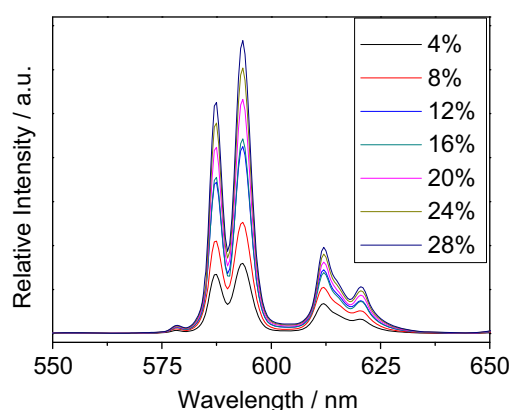
Table 1
The ratios of luminescence intensity at 594 and 613 nm.

Concentration of Eu (mol%)	4	8	12	16	20	24	28
Intensity (594 nm)	79.68	126.5	212.5	221.4	266.4	302.1	333.1
Intensity (613 nm)	33.94	52.49	72.49	69.39	81.30	90.38	97.97
I_{594}/I_{613}	2.348	2.410	2.931	3.191	3.277	3.342	3.440
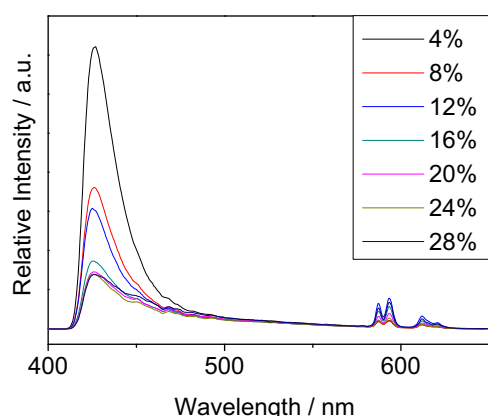
Fig. 5. Emission spectra of $Sr_{3(1-x)}P_4O_{13}$: $3x$Eu ($\lambda_{ex}=334$ nm, $x=0.04$–0.28).
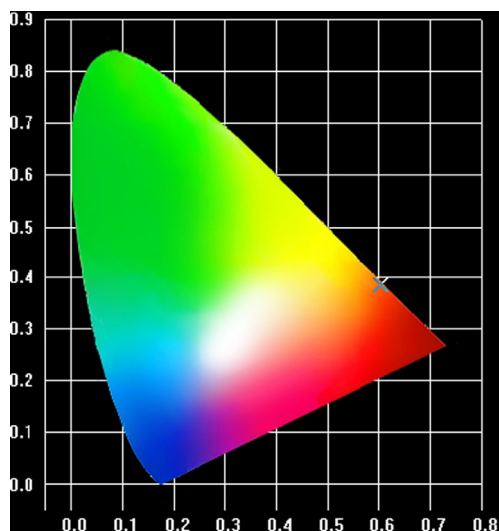

Fig. 6. CIE chromaticity diagram of $Sr_3P_4O_{13}$: Eu phosphors.

20 to 28 mol%. The decrease of Eu^{2+} photoluminescence intensity may be explained by the fact that the $[V_{Sr}]$ vacancies also increase with increasing Eu concentration and excess Eu^{3+} ions would occupy the position of $[V_{Sr}]''$. The $[V_{Sr}]''$ vacancy with two negative charge was changed into a positive charge so that it cannot offer charge to Eu^{3+} and the reduction was impeded. In order to keep electroneutrality, the compound has to absorb O^{2-} from air and form Eu_2O_3. So the reduction degree and the crystallization of $Sr_3P_4O_{13}$ decrease, which is consistent with the results of XRD.

3.4. The CIE chromaticity coordinates of the phosphors

The CIE chromaticity coordinates of the $Sr_3P_4O_{13}$: Eu phosphors have been calculated from the PL spectra under the excitation of 394 nm. The color coordinates on the CIE chromaticity diagram are shown in Fig. 6. The chromaticity coordinates of all the prepared samples are located in the orange–red light region. The CIE chromaticity coordinates scarcely show any change with the increasing Eu concentration, which indicates that

Table 2
CIE chromaticity coordinates of $Sr_3P_4O_{13}$: Eu phosphors.

Concentration of Eu (mol%)	4	8	12	16	20	24	28
x	0.604	0.605	0.603	0.602	0.602	0.602	0.602
y	0.385	0.385	0.386	0.387	0.387	0.387	0.388

the color stability of $Sr_3P_4O_{13}$: Eu is good. The CIE chromaticity coordinates are listed in Table 2.

4. Conclusion

In this work, a new orange–red emitting phosphor of $Sr_3P_4O_{13}$: Eu was prepared by the conventional solid-state reaction at 1000 °C and its photoluminescence properties were investigated. The PL emission spectrum consists of a broad band emission around 427 nm ascribed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} for the self-reduction of Eu^{3+} in the $Sr_3P_4O_{13}$ crystal structure and line emissions at 588, 594, 613, 654 and 703 nm resulted from the $^5D_0 \rightarrow {}^7F_J$ ($J=1$, 2, 3, and 4) transitions of Eu^{3+} ions, respectively. The incomplete self-reduction of Eu^{3+} to Eu^{2+} in $Sr_3P_4O_{13}$ prepared in air is explained with the charge compensation mechanism. The phosphor exhibits efficient orange–red emission excited by 394 nm light and excellent color stability, indicating that it has favorable properties for application as an NUV LED conversion phosphor.

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