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Synthesis and photoluminescence of Eu^{2+} by co-doping Eu^{3+} and Cl^- in $Sr_2P_2O_7$ under air atmosphere

Fuhe Le[a,b,c], Luxiang Wang[a,b,c], Wei Jia[a,b,c], Dianzeng Jia[a,b,c,*], Shujuan Bao[a,b,c]

[a] Key Laboratory of Material and Technology for Clean Energy, Ministry of Education, Xinjiang University, Urumqi 830046, Xinjiang, China
[b] Key Laboratory of Advanced Functional Materials, Autonomous Region, Xinjiang University, Urumqi 830046, Xinjiang, China
[c] Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, Xinjiang, China

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ABSTRACT

A novel phosphor $Sr_2P_2O_7$ co-doped with europium ion and chlorine ion was firstly synthesized by solid state reaction under air atmosphere. Its properties were systematically analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and fluorescence spectra. The introduction of chlorine into the system was helpful and necessary to Eu^{3+} substitute Sr^{2+} site and subsequently to reduce Eu^{3+} to Eu^{2+}, XPS results confirmed that some amount of Eu^{3+} ions could be reduced to Eu^{2+} ions under air atmosphere at high temperature. The reduction tendency of Eu^{3+} depends not only on the doping Cl^- content, but also on the sintering temperature and time. Photoluminescence spectra also revealed that europium ions were present in divalent as well as trivalent oxidation states, the emission peak at 415 nm is ascribed to the typical 5d–4f transition of Eu^{2+}, 592 nm and 613 nm assigned to the characteristic transitions of $^5D_0$–$^7F_{1,2}$ of Eu^{3+}. Such abnormal reduction was attributed to the electronegative defects formed by nonequivalent substitution of Eu^{3+} on the Sr^{2+} sites in the investigated phosphors.

1. Introduction

Luminescent materials have sparked significant attention for their practical and promising applications in LED, display devices and bioluminescence [1–6]. In particular, divalent europium-doped phosphors have been investigated extensively because the intense visible and wide range emission from 400 to 700 nm depending on the crystal field of the host materials is applicable for various lighting devices [7–11]. Generally, the Eu_2O_3 is employed as the starting material, in which trivalent europium is then reduced to its divalent state in reducing ambience (CO, H_2 or H_2/N_2), this will need special equipments and enhance the danger and cost for obtaining the kinds of phosphors. Whereas, Täle et al. [12] has indicated the possibility of synthesizing phosphors activated with Eu^{2+} under air atmosphere at high temperature. Up to now, the reduction of Eu^{3+} to Eu^{2+} occurred in some matrixes at high temperatures in air has been reported, such as ZnP_2O_7 [13], SrB_4O_7 [14], $CaBPO_5$ [15], $Ba_2(PO_4)_3$ [16], $BaZnSiO_4$ and $Sr_4Al_{14}O_{25}$ [17]. Pei systemically investigated the abnormal reduction of Eu^{3+} to Eu^{2+} in air at high temperature and found that Eu^{3+} could be reduced to its divalent state in air only in some hosts contained a three-dimensional (3-D) network structure, formed by the corner sharing anionic tetrahedron, when Eu^{3+} substituted the cations in the host [18]. The α-$Sr_2P_2O_7$ has an orthorhombic crystal structure with *Pnma* space group and is built up by PO_4 tetrahedrons [19]. In this structure, two kinds of PO_4 tetrahedrons are linked to each other by corner sharing to form a 3-D network structure and each strontium atom coordinates nine terminal oxygen atoms from five different P_2O_7 groups, so it is possible that Eu^{3+} could be reduced in α-$Sr_2P_2O_7$ under air atmosphere. Yet, this reduction has not been reported in the case of singly Eu^{3+} doped α-$Sr_2P_2O_7$. van der Voort [20] and Doat [21] reported that the solubility of Eu^{3+} ions in pyrophosphate is limited and even at a small quantity of doped Eu^{3+} a second $EuPO_4$ phase would be observed. The problem hinder the reduction from Eu^{3+} to Eu^{2+} in air is that Eu^{3+} cannot easily enter into the α-$Sr_2P_2O_7$ host and substitute the Sr^{2+}.

In order to solve this problem, it must find a way to introduce Eu^{3+} into the α-$Sr_2P_2O_7$ host. In this paper, the chlorine was chosen as an anionic dopant, the effects of Cl^- doping on the properties of α-$Sr_2P_2O_7$:Eu^{3+} were studied in detail. The results indicated that the doping of Cl^- contributes to incorporate Eu^{3+} into Sr^{2+} site in $Sr_2P_2O_7$ host by increasing unit cell volume of the as-prepared samples, which results in the partial reduction of Eu^{3+} to Eu^{2+} in the investigated phosphors.

2. Experimental details

$Sr_{2(1-x)}P_2O_7$:$2x$Eu, $y$$Cl^-$ (x, y represent the Eu/(Eu + Sr) and Cl/(Eu + Sr) atomic ratios respectively) powder samples were synthesized by a high temperature

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* Corresponding author at: Key Laboratory of Material and Technology for Clean Energy, Ministry of Education, Xinjiang University, Urumqi 830046, Xinjiang, China. Tel.: +86 991 8580032; fax: +86 991 8580032.
E-mail addresses: jdz0991@gmail.com, jdz@xju.edu.cn (D. Z. Jia).

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solid-state reaction. Stoichiometric amount of $Sr(NO_3)_2$, $SrCl_2$, Eu_2O_3 and $(NH_4)_2HPO_4$ were used as raw materials. These starting materials were ground and mixed homogeneously in an agate mortar and sintered in alumina crucibles at different temperatures in air. The samples were then naturally cooled down to room temperature. Finally, the as-prepared samples were ground to powders for the structure and spectral measurements.

The structures of the as-prepared samples were identified by MAC Science MXP18AHF X-ray diffractometer with graphite-monochromatized Cu Kα radiation. XPS data for the europium and chlorine co-doped strontium pyrophosphate were collected with an AXIS Ultra instrument from Kratos Analytical, using Al Kα radiation as the excitation source. All the binding energies were calibrated by using the carbon 1s line (C 1s = 284.6 eV) as a reference. Photoluminescence excitation (PLE) and emission (PL) spectra were measured with a HITACHI F-4500 spectrometer equipped with a 150 W xenon lamp as the excitation source. All the measurements were carried out at room temperature.

3. Results and discussion

The optical properties of europium ion activated materials strongly depend on its valence states. Normally, Eu^{3+} can emit the light from orange to red, which are originated from 4f–4f transitions of Eu^{3+}. However, the efficiency of this type of luminescent materials is supposed to be very low, since the 4f–4f transitions of Eu^{3+} are forbidden transitions and their excitations are very ineffective in $Sr_2P_2O_7$ host; for most Eu^{2+} ion doped phosphors, the stimulated emission are originated from 4f–5d transitions and their emission color can vary in a brand range from ultraviolet to red. Because the 4f–5d transitions of Eu^{2+} are allowed transitions, the absorption and emission of Eu^{2+} in many hosts are very efficient, which makes the Eu^{2+}-activated luminescent materials to be good candidates for industrial phosphors.

3.1. Phase analysis

In order to study the chemical states of europium in $Sr_{1.98}P_2O_7$:0.02Eu, $0.12Cl^-$ phosphor, the europium 3d XPS spectrum is shown in Fig. 1. There obviously exists two peaks around 1124 and 1135 eV, the shapes and the binding energies of the Eu 3d singles in $Sr_{1.98}P_2O_7$:0.02Eu, $0.12Cl^-$ phosphor agree well with the signals of Eu^{2+} $3d_{5/2}$ and Eu^{3+} $3d_{5/2}$, respectively [22]. Thus, the coexistence of Eu^{2+} and Eu^{3+} in the $Sr_{1.98}P_2O_7$:0.02Eu, $0.12Cl^-$ phosphors can be inferred from the XPS spectrum.

Fig. 2 shows the characteristic X-ray diffraction patterns of the synthesized europium and chlorine substituted strontium pyrophosphate. The diffraction peaks of the doped samples are very similar to those of the undoped one and display a major structure of α-$Sr_2P_2O_7$ (JCPDS No. 24-1011). However, when compared to the undoped sample carefully, an additional low-reflection can be both observed in the two doped ones at 31.8° which is assigned to the (1 1 2) reflection of $EuPO_4$ (JCPDS No. 25-1055). For $Sr_{1.98}P_2O_7$:0.02Eu, $0.12Cl^-$, the reflection intensity of $EuPO_4$ is obvious weaker than that of $Sr_{1.98}P_2O_7$:0.02Eu. It can be explained that more Eu^{3+} ions may dope into lattice of $Sr_2P_2O_7$ with the introduction of Cl^-.

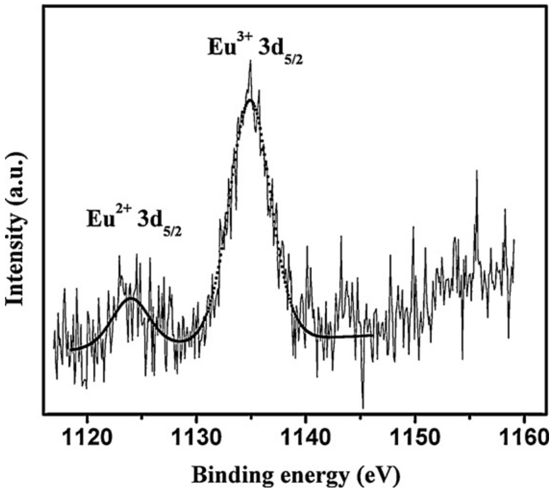

Fig. 1. XPS 3d spectrum of Eu in $Sr_{1.98}P_2O_7$:0.02Eu, $0.12Cl^-$ phosphor.

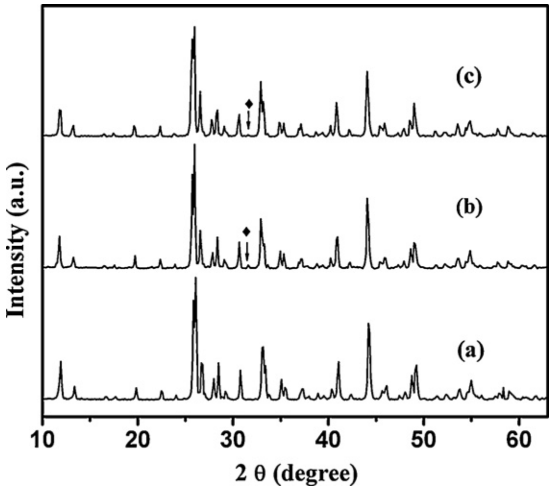

Fig. 2. The XRD patterns of (a) $Sr_2P_2O_7$, (b) $Sr_{1.98}P_2O_7$:$0.02Eu^{3+}$, (c) $Sr_{1.98}P_2O_7$:0.02Eu, $0.12Cl^-$ sintered at 1100 °C for 2 h. ♦: $EuPO_4$.

The lattice parameters and the unit cell volumes of the as-prepared phosphors were calculated from the diffraction data and are listed in Table 1. It can be seen that doping of Eu^{3+} in $Sr_2P_2O_7$ results in a slight shrinkage of the unit cell volume. On the other hand, the unit cell volume of $Sr_{1.98}P_2O_7$:0.02Eu, $0.12Cl^-$ phosphor increases when monovalent chlorine was used as another dopant. The increase in volume in comparison with the undoped sample is related to the atom size effect, it is commonly accepted that Eu ions and Cl^- are proposed to substitute the Sr^{2+} and O^{2-}, respectively. Because the ionic radii of Eu^{2+} (1.17 Å) which were reduced from Eu^{3+} by the doping of Cl^- and Eu^{3+} (1.07 Å) are smaller than that of Sr^{2+} (1.26 Å), the doping of Eu^{3+} and Eu^{2+} ions will decrease the volume of the investigated sample [23]. On the contrary, since the atom radius of chlorine is bigger than that of oxygen, the doping of chlorine will increase the volume of the sample. These results imply that chlorine does enter into the host lattice.

3.2. The luminescent properties of $Sr_{2(1-x)}P_2O_7$:2xEu, yCl^-

3.2.1. The excitation and emission spectra

The UV excited photoluminescence spectra of $Sr_{1.98}P_2O_7$: 0.02Eu, $0.12Cl^-$ sintered at 1100 °C for 2 h are depicted in Fig. 3. The emission spectrum, excited by 260 nm UV light (Fig. 3b), shows weak lines centered at 592 nm and 613 nm which can be ascribed to the $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions of Eu^{3+}, respectively [24]. At the same time, monitoring the 592 nm emission, the corresponding excitation spectrum (Fig. 3a) consists of a brand band centered at 260 nm (originated from Eu^{3+}–O^{2-} charge transfer transition) and a group of sharp lines (originated from 4f–4f transitions of Eu^{3+}) [25]. The relative intensities of the different transitions and the positions of the different components appeared in luminescence

Table 1
Lattice parameters of the obtained samples.

Sample	*a* (Å)	*b* (Å)	*C* (Å)	Unit cell volume (Å^3)
$Sr_2P_2O_7$	8.917	13.173	5.400	634.304
$Sr_{1.98}P_2O_7$:$0.02Eu^{3+}$	8.911	13.164	5.403	633.796
$Sr_{1.98}P_2O_7$:0.02Eu, $0.12Cl^-$	8.904	13.230	5.423	638.829

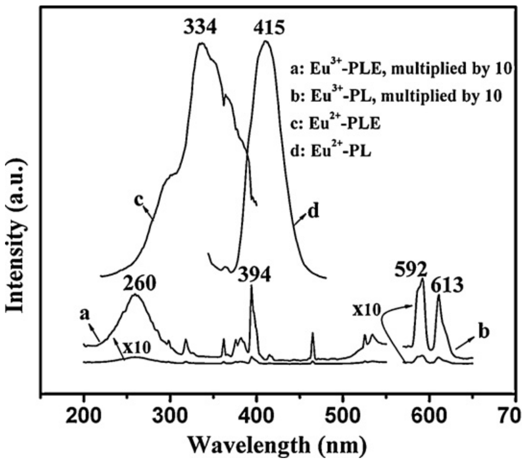

Fig. 3. The photoluminescence spectra of $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl$^-$ sintered at 1100 °C for 2 h. Excitation spectra: (a) λ_{em} = 592 nm and (c) λ_{em} = 415 nm; emission spectra: (b) λ_{ex} = 260 nm and (d) λ_{ex} = 334 nm.

spectra of Eu^{3+} resemble those of $EuPO_4$ [26]. It confirms that $EuPO_4$ could exist in $Sr_2P_2O_7$ phases; this is also in agreement with the result obtained by XRD. Meanwhile, another excitation spectrum recorded under emission at 415 nm in the range of 250–400 nm (Fig. 3c) is due to the 4f–5d transition of the Eu^{2+} [27]. Emission spectrum from the $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl$^-$ phosphor obtained after 334 nm excitation is shown in Fig. 3d and it exhibits an emission peaked at 415 nm, a well-known characteristic of Eu^{2+} 5d–4f transition [28]. The above results confirm the co-presence of Eu^{3+} and Eu^{2+} in $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl$^-$ phosphor. It can be concluded that partial reduction of Eu^{3+} to Eu^{2+} has taken place in $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl$^-$ phosphor prepared in air at high temperature. The result is also in accordance with the previous XPS results.

The emission spectrum excited by 334 nm and the excitation one monitored the emission at 415 nm of $Sr_{1.98}P_2O_7$:0.02Eu were also detected (see Fig. 4), it is found that the 5d–4f transition emission of Eu^{2+} cannot be observed as well as the 4f–5d transition absorption in Eu^{3+} singly doped $Sr_2P_2O_7$ sample. And only the weak and characteristic emission peaks of Eu^{3+} present when the sample excited by 260 nm (same to that of in Fig. 3b). Therefore, it reveals clearly that the reduction from Eu^{3+} to Eu^{2+} can not occur in the absence of chlorine in $Sr_2P_2O_7$ host in air.

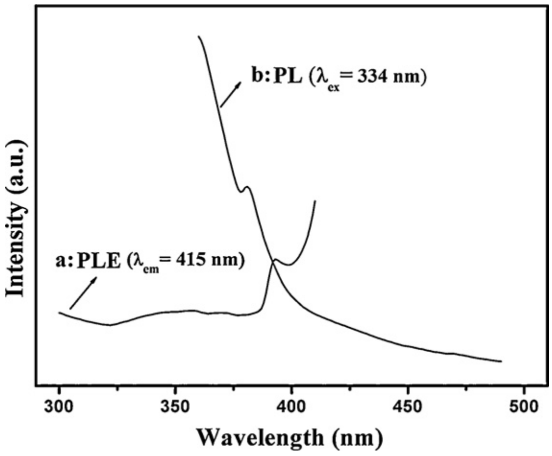

Fig. 4. the excitation (a) and emission (b) spectra of $Sr_{1.98}P_2O_7$:0.02Eu^{3+} sintered at 1100 °C for 2 h.

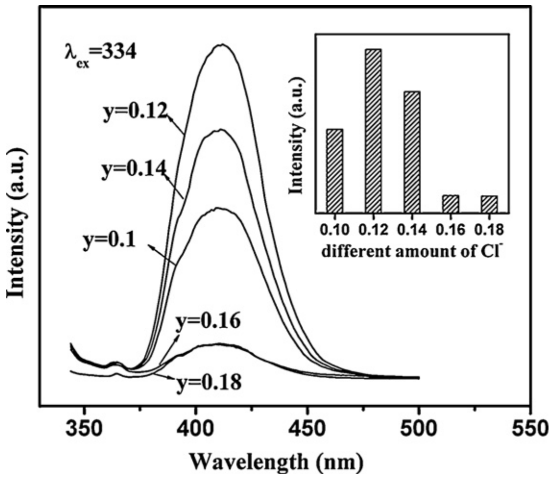

Fig. 5. Emission spectra of $Sr_{1.98}P_2O_7$:0.02Eu, yCl$^-$ sintered at 1100 °C for 2 h.

3.2.2. Influence of the doping concentration

In order to find the critical concentration of Cl$^-$ in the investigated phosphors, the emission spectra of $Sr_{1.98}P_2O_7$:0.02Eu, yCl$^-$ phosphors with various Cl$^-$ concentrations are presented in Fig. 5. These spectra show a broad band from 380 to 480 nm with a peak occurring at 415 nm, these similar spectra profiles are indicative of the same kind emission center of Eu^{2+}. It can be seen that the strongest luminescence can be reached when the Cl$^-$ content is 0.12. The luminescence intensity dramatically decreases with further increasing Cl$^-$ contents in the investigated phosphors, and it is related to the increasing defects of $Cl_O^{\bullet}$ created by the substitution of divalent oxygen with monovalent chlorine.

Another series of $Sr_{2(1-x)}P_2O_7$:2xEu, 0.12Cl$^-$ phosphors with various europium contents were synthesized and their emission spectra are given in Fig. 6. The shapes of these spectra are also similar. When x = 0.01, the emission intensity reaches the maximum value. A further increase in the europium concentration leads to a decrease in the emission intensity, which may be ascribed to the concentration quenching of Eu^{2+}.

3.2.3. Influence of sintering temperature and sintering time

The emission spectra of $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl$^-$ synthesized at different temperatures (1000–1200 °C) for 2 h are presented in Fig. 7. Obviously, in case of that sintering temperature is too low, the diffusion rate of Eu^{3+} is low, which will hinder Eu^{3+} enter into the host and further decrease the possibility of the reduction of Eu^{3+}

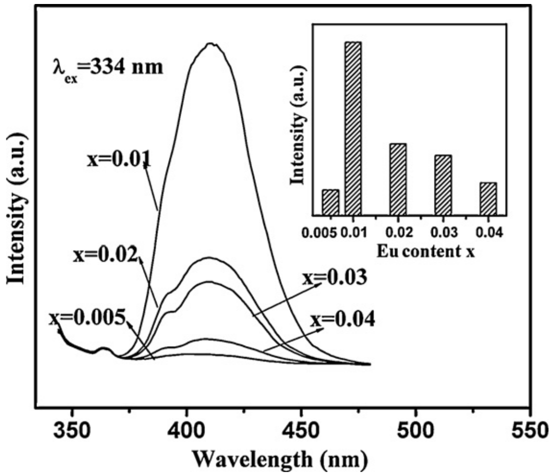

Fig. 6. Emission spectra of $Sr_{1.98}P_2O_7$:2xEu, 0.12Cl$^-$ sintered at 1100 °C for 2 h.

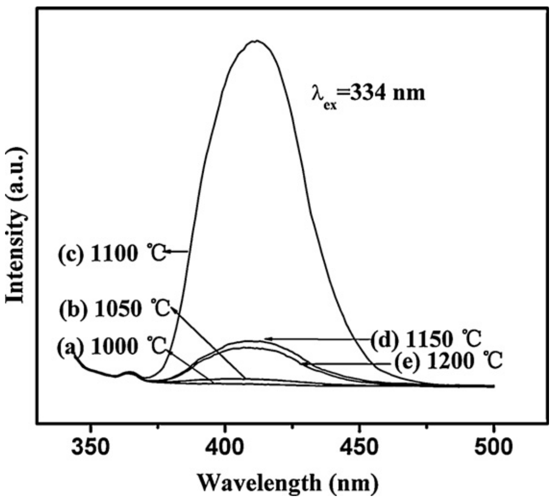

Fig. 7. Emission spectra of $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl^- sintered at 1000–1200 °C.

to Eu^{2+}. It is observed that Eu^{3+} ions begin to reduce into Eu^{2+} ions when the sintering temperature is higher than 1050 °C. It is evidenced by the Eu^{2+} broad emission peaked at 415 nm. Compared to the samples obtained at other temperatures, this emission intensity is significantly enhanced at 1100 °C. And it then begins to decrease drastically when the phosphor is sintered at a higher temperature. It may be related to reoxidization of some Eu^{2+} into Eu^{3+} again.

To reveal the optimal sintering time for synthesis of the investigated phosphors, The emission spectra of $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl^- obtained for different sintering time at a fixed 1100 °C temperate are shown in Fig. 8. It can be seen the emission intensity of Eu^{2+} increase with the sintering time from 0 to 2 h. When the sintering time prolongs further, the emission intensity begins to decline. It is possible that the reoxidization of Eu^{2+} to Eu^{3+} appears when the sintering time increases.

3.2.4. The mechanism of the reduction from Eu^{3+} to Eu^{2+}

The abnormal reduction phenomenon of Eu^{3+} to Eu^{2+} in $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl^- phosphors synthesized in air can be explained by means of charge compensation principle [18]. In general, the doped Eu^{3+} would substitute Sr^{2+} in the host lattice. In order to keep the electrical neutrality of the compound, two Eu^{3+} ions should substitute three Sr^{2+} ions. Therefore, one negative defect V''_{Sr} and two positive defects of $Eu^{\bullet}_{Sr}$ would be created by each substitution of every two ions in the compound. Consequently, by thermal stimulation, the negative charges in V''_{Sr} defects would be transferred to and captured by the defects of $Eu^{\bullet}_{Sr}$, which results in the reduction of Eu^{3+} to Eu^{2+}. α-$Sr_2P_2O_7$ phase has a 3D-netwok structure, where [P_2O_7] groups connect with each other by corner sharing and Sr^{2+} ions locate at the polyhedra form in the P–O network [19]. Every Eu^{2+}, in this structure, is completely surrounded by terminal oxygen atoms from diphosphate groups; therefore the 3-D network structure keeps Eu^{2+} away from being reoxidized in air at high temperature. The reduction form could be described as the following equation:

$$2Eu^{\bullet}_{Sr} + V''_{Sr} = 2Eu^{\times}_{Sr} + V^{\times}_{Sr}$$

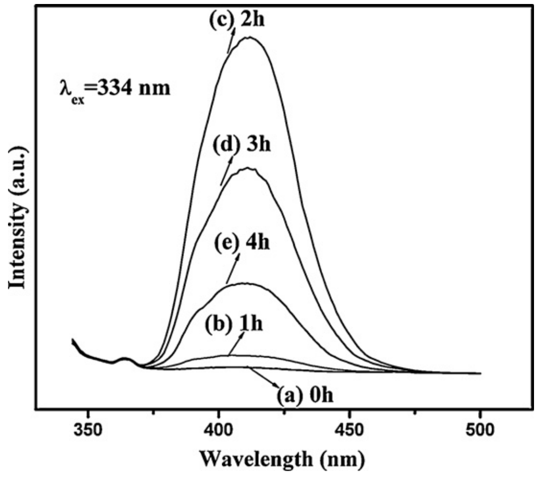

Fig. 8. Emission spectra of $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl^- sintered at 1100 °C for different hours.

It can be concluded that the necessary requirements for the reduction of Eu^{3+} to Eu^{2+} are that Eu^{3+} ions must substitute for Sr^{2+} ions and occupy the Sr^{2+} sites in the investigated phosphors. Since the substitution of Sr^{2+} with Eu^{3+} in pyrophosphate is difficult, it is impossible to reduce Eu^{3+} to Eu^{2+} in the Eu^{3+}-doped $Sr_2P_2O_7$ in air. However, with the chlorine substitution for oxygen, the unit cell volume of the $Sr_2P_2O_7$ host increases, it makes the introduction of Eu^{3+} into the Sr^{2+} sites easier, so the Eu^{3+} can be reduced to its divalent state in the investigated phosphors in air. But, considering that increasing the concentration of chlorine can probably compensate for defects of V''_{Sr}, the appropriate doping quantity of Cl^- should be taken to yield considerable phosphor.

4. Conclusions

In summary, a $Sr_2P_2O_7$ phosphor doped with Eu^{3+} and Cl^- was prepared in air by a high temperature solid state routine. It was found that the introduction of Cl^- makes the unit cell volume of strontium $Sr_2P_2O_7$ get bigger and can help Eu^{3+} to enter into the Sr^{2+} lattice sites easily. Both XPS and photoluminescence measurements suggested the reduction of Eu^{3+} to Eu^{2+} can be realized in air atmosphere at high temperature. In comparison with the Eu^{3+} singly doped sample, it can be found that Eu^{2+} could be obtained only when the Cl^- dopant is present in the system. Furthermore, the optimal sintering conditions for preparing $Sr_{1.98}P_2O_7$:0.02Eu, 0.12Cl^- phosphors in air were found to be 1100 °C for 2 h.

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