Hydrothermal synthesis and luminescent properties of Sb^{3+}-doped $Sr_3(PO_4)_2$

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Abstract

Sb^{3+}-doped $Sr_3(PO_4)_2$ crystals has been synthesized using phosphoric acid, strontium hydroxide and antimony powder as the raw materials through a hydrothermal reaction method. The crystallinity and the microstructure were investigated using X-ray diffraction and scanning electron microscopy. The photoluminescent property was investigated using luminescent spectrometer. Phase pure $Sr_3(PO_4)_2$ crystal was obtained and it has a shape of hexagonal rod. It showed the emission and excitation peaks at 396, 250, and 215 nm, respectively, indicating that the emission is attributed to $^3P_1$–$^1S_0$ transition and the excitation is attributed to $^1S_0$–$^3P_1$ and $^1S_0$–$^1P_1$ transition. It was also observed that the intensity of photoluminescence is thermally stable up to 673 K.
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1. Introduction

Recently, considerable interest has been focused on the preparation of inorganic phosphor materials because they have been used as various types of display panels, such as plasma display panel (PDP), vacuum fluorescent display (VFD), and field emission display (FED) [1–3]. Sb^{3+} and Mn^{2+} co-activated calcium halophosphates have been used in fluorescent lamps for a long time [4]. There have been many reports on the preparation of luminescent materials that used orthophosphates as a host [5–7]. Kroger [8] investigated the preparation of orthophosphates of calcium and strontium with double

activators. Froelich and Margolis [9] also studied calcium orthophosphate activated by cerium and manganese, which emits deep red light. Butler [10] described some alkaline earth orthophosphate phosphors consists of calcium, strontium and barium. Sarver and coworkers [11] reported the luminescence of tin activated strontium orthophosphate. Koelmans and Cox [12] also investigated the luminescence of modified tin activated strontium orthophosphate and found that modified tin activated $Sr_3(PO_4)_2$ could give a strong red luminescence with a maximum peak at about 630 nm under excitation with 253.7 nm. Blasse and coworkers [13] discussed the luminescence of Sb^{3+} activated LPO_4 (L = Sc, Lu, Y) and found that existed a Jahn–Teller effect in the emission and excitation spectra of the Sb^{3+} ion in the above compounds.

Though there have been many reports about the synthesis and characterization of luminescent materials as described above, all the materials were synthesized by high temperature solid-state reaction method. This

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method has disadvantage of expensive and high temperature process. The reaction products are easy aggregated and to be contaminated. However, high quality crystals of which size can be controlled are easy to be obtained in the hydrothermal system where the reaction condition is milder compare with the solid-state method. It can also change the atmosphere in the hydrothermal system and to obtain a compound that consists of elements with special valence. In additional, chemical doping in this system is also easy to be done. Because of the advantages described above, hydrothermal synthesis has been used to prepare phase-pure, high-quality ceramic (oxides) materials and has made great success in the synthesis of zeolites and other micro- and mesoporous materials [14]. Recently, the hydrothermal synthesis of phosphors has attracted considerable interests [15–19]. Rao [15] and coworkers has prepared Eu^{2+} activated strontium aluminates by hydrothermal method and investigated the luminescence in 1990. Li et al. [20] synthesized Mn^{2+}-doped Zn_2SiO_4 that was mainly used as a green phosphor in lamps and cathode ray tubes by hydrothermal method and investigated the relationship between the morphologies and the additional ions. Haase et al. [16] prepared doped colloidal nanoparticles of YVO_4:Ln (Ln = Eu, Sm, Dy) by hydrothermal method and studied their luminescent properties. In 1999, doped colloidal nanomaterials of $LaPO_4$:Eu, $LaPO_4$:Ce and $LaPO_4$:Ce,Tb have been prepared through a hydrothermal method by Haase et al. [17]. Sb^{3+}-doped and Sb^{3+} and Mn^{2+} co-doped hydroxyapatite were synthesized from hydrothermal system by Chen et al. [21] and investigated the luminescent properties of Sb^{3+} and Mn^{2+} in the compounds. And the energy transfer from Sb^{3+} ion to Mn^{2+} ion was observed.

The luminescent property of Sb^{3+}-doped rare-earth phosphates [7,13] which were prepared by traditional solid-state method has been widely investigated. While, the research about Sb^{3+}-doped phosphates has not been reported which were obtained from hydrothermal system. It has been reported that Sb^{3+} ion could take only the crystallographic position of Y^{3+} ion in YPO_4, which is octahedrally coordinated by six oxygen anions [13]. However, there are two crystallographic positions for the Sr^{2+} ion in the structure of $Sr_3(PO_4)_2$: one position is coordinated by six oxygen anions and the other is coordinated by ten oxygen anions [22]. However, as it was observed in our experiment, the emission and excitation spectrum of the Sb^{3+}-doped $Sr_3(PO_4)_2$ crystal is similar with that Sb^{3+}-doped YPO_4. We may consider the Sb^{3+} ion takes the 6-coordianted Sr^{2+} position in the $Sr_3(PO_4)_2$ crystal. Because the Sb^{3+} in YPO_4 and $Sr_3(PO_4)_2$ is coordinated by six oxygen anions, the current results on Sb^{3+}-doped $Sr_3(PO_4)_2$ will be compared with Sb^{3+}-doped YPO_4 reported by Grafmeyer [7] and Blasse [13].

In this article, Sb^{3+}-doped $Sr_3(PO_4)_2$ crystal was synthesized from hydrothermal system and the photoluminescent property of Sb^{3+} ion in $Sr_3(PO_4)_2$ crystal was investigated at the room temperature. The thermal stability of this luminescent material was discussed and found it can be used as blue phosphor material.

2. Experimental

The starting materials for the synthesis of Sb^{3+}-doped $Sr_3(PO_4)_2$ crystal were $Sr(OH)_2 \cdot 8H_2O$ (A.R.), 85% H_3PO_4 (G.R.) and antimony powder (A.R.). In a typical synthesis procedure, an initial mixture with a molar composition of 1.5 $Sr(OH)_2$:H_3PO_4:0.01 Sb:156 H_2O was stirred till homogeneous, sealed in a Teflon-lined stainless steel autoclave and heated at 513 K for 10 days. The reaction product was washed thoroughly with distilled water and dried at room temperature.

The phase of the powder was identified using the powder X-ray diffraction (XRD) (Siemens D5005) with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The particle morphologies of the crystals were observed by scanning electron microscopy using a Hitachi X-650 scanning electron microscope. The luminescent property of the samples was investigated using a Perkin-Elmer Luminescence Spectrometer-Ls55. In order to obtain good spectral resolution, a slit width of 5.0 nm was selected for both excitation and emission measurements.

## 3. Results and discussion

3.1. Crystallinity and microstructure

Fig. 1(a) shows the XRD pattern of the sample synthesized using the hydrothermal method and the simulated X-ray diffraction of $Sr_3(PO_4)_2$ powder using the data of ICSD [22] and Fig. 1(b) displays the scanning electron microscopy (SEM) image of Sb^{3+}-doped $Sr_3(PO_4)_2$ crystals. The diffraction peaks of the synthesized powder obtained in our experiment are well consistent with those of simulated pattern, indicating that $Sr_3(PO_4)_2$ pure phase was obtained. The morphology of the crystal is hexagonal flake and the diameter of the flake is about 10–20 μm and the length of the powder is in the range between 30 and 50 μm as shown from the SEM picture.

3.2. Photoluminescence characteristics

Fig. 2 shows the excitation and emission spectra of Sb^{3+}-doped $Sr_3(PO_4)_2$ crystal measured at room temperature. The range of the emission band is from 300 to 500 nm with the peak at about 396 nm. The full-width at half-maximum of the emission peak is about
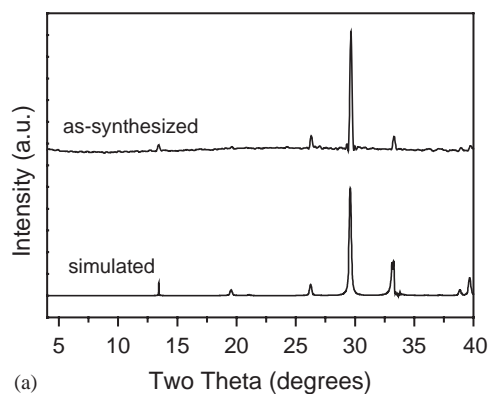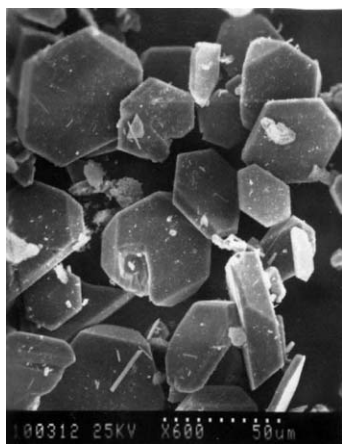
Fig. 1. Powder X-ray diffraction patterns of as-synthesized and simulated of $Sr_3(PO_4)_2$ (a) and scanning electron photograph of $Sr_3(PO_4)_2$ (b).
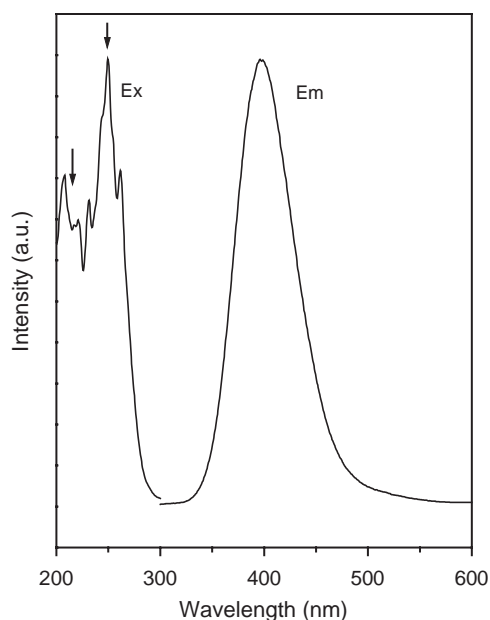

Fig. 2. Photoluminescent spectra of Sb^{3+}-doped $Sr_3(PO_4)_2$ measured at room temperature. For emission measurement, the excitation wavelength was 250 nm whereas for excitation measurement the emission wavelength was 396 nm.

65 nm and it is very close to the 60 nm of famous blue light materials $Ba_{0.95}Mg_{0.2}Al_{10.8}O_{17.2}$ [23]. The excitation spectrum consists of two bands as pointed out with arrows: a doublet band around 215 nm and a triplet band around 250 nm in which the latter is the main excitation band. And this is very different from that obtained through traditional solid-state method. The positions of the both absorption bands are located at 222.6 and 294 nm, respectively, and the intensity of the former is stronger than the latter in the absorption spectrum of the sample synthesized by traditional method. The investigation of the affection on luminescent properties of two different methods is in process. However, the position and the relative intensity of the excitation band of the title compound is similar with that reported Sb^{3+}-doped $Ca_5(PO_4)_3OH$ obtained from the hydrothermal system earlier [21].

Both Grafmeyer [7] and Blasse [13] investigated the luminescence property of Sb^{3+}-doped YPO_4 which was prepared through the solid-state method. And two emission bands with peaks at about 300 and 395 nm were observed at room temperature in each of their experiments. Grafmeyer [7] reported that the excitation spectrum consisted three bands in the range from 220 to 250 nm, while Blasse [13] found that it consisted only two bands: a doublet band around 238 nm and a triplet band around 200 nm in the excitation spectrum of Sb^{3+}-doped YPO_4. The luminescent property of our as-synthesized Sb^{3+}-doped $Sr_3(PO_4)_2$ sample through hydrothermal method is different from those reports. Only one emission band around at 396 nm was observed at room temperature and the excitation spectrum consists two bands but the position is different from that reported data by Blasse [13].

According to Blasse [13], the energy level of ground state of Sb^{3+} $(5s^2)$ is $^1S_0$, the $5s5p$ excited state configuration gives rise to the triplet levels $^3P_0$, $^3P_1$, $^3P_2$ and a singlet level $^1P_1$ when the Sb^{3+} ions are octahedrally coordinated by six anions. The transition $^1S_0 \rightarrow {}^3P_0$ is strongly forbidden and the transition $^1S_0 \rightarrow {}^3P_1$ becomes partially forbidden. The transition $^1S_0 \rightarrow {}^3P_2$ is forbidden, but can be induced by coupling of the $^3P_2$ level to non-totally symmetric lattice vibrations. The only allowed transition is $^1S_0 \rightarrow {}^1P_1$ [23]. Fig. 3 shows a simple schematic diagram showing the energy levels of the Sb^{3+} in $Sr_3(PO_4)_2$ crystal. Therefore, the doublet band around 215 nm should be assigned to the $^1S_0 \rightarrow {}^1P_1$ transition and the triplet band around 250 nm should be attributed to the $^1S_0 \rightarrow {}^3P_1$ transition, and the emission band around 396 nm should be assigned to the $^3P_1 \rightarrow {}^1S_0$ transition of the Sb^{3+} ion.

It has been known that the luminescent properties of the Sb^{3+} ion strongly depend on the crystallographic position in the host crystal [24,25]. The position of the emission band of Sb^{3+} ion shifted much with little F^- and Cl^- anions added into the calcium phosphate
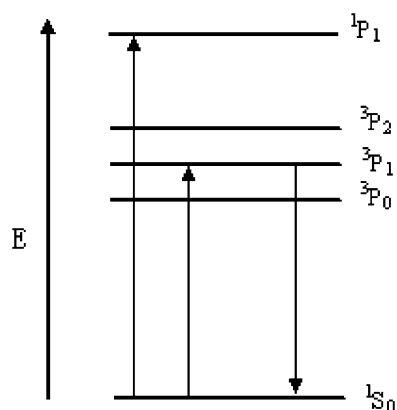
Fig. 3. The simple schematic diagram of energy levels of the Sb^{3+} in $Sr_3(PO_4)_2$ crystal.

Fig. 4. Relationship of the luminescent intensity of Sb^{3+}-doped $Sr_3(PO_4)_2$ and the calcined temperature.

system [21]. It is well known that only one crystallographic position is available for the Sb^{3+} ion in YPO_4 with a tetragonal zircon structure [13]. However, there are two crystallographic positions for the Sr^{2+} ion in the structure of $Sr_3(PO_4)_2$. Therefore, the Sb^{3+} ions could replace one of or both of the two possible positions of the Sr^{2+} ions in the structure of $Sr_3(PO_4)_2$ when Sb powder was added into the hydrothermal reaction system. However, as it was observed in our experiment, there is only one emission band in the spectrum of the Sb^{3+}-doped $Sr_3(PO_4)_2$ crystal. This result shows that the Sb^{3+} ion occupies only the 6-coordinated Sr^{2+} position or occupies both positions but the other position of Sb^{3+} cannot emit. As far as we know, the emission of Sb^{3+} in a 10-coordinated position has not been reported. And in the other hand, our experimental results of excitation and emission spectrum show very similar to those reported by Grafmeyer [7] and Blasse [13], we may conclude that the Sb^{3+} ion take the 6-coordianted Sr^{2+} position in the $Sr_3(PO_4)_2$ crystal. Therefore, it can also be explained by Jahn-Teller effect why there are two excitation bands in our experiment as observed in the excitation spectrum of the Sb^{3+} ions in different systems [26–28].

There should be required charge compensation when the trivalent Sb^{3+} ion take the bivalent Sr^{2+} ion position in the $Sr_3(PO_4)_2$ crystal for balancing the charge. And this will lead to the aberration in the SbO_6 octahedron in the $Sr_3(PO_4)_2$ crystal. This may be one of the reasons why there is difference in the spectra between ours and those of reported by Grafmeyer [7] and Blasse [13]. We consider that it is the hydrothermal method and the host lattice that leads to the difference of luminescent property of Sb^{3+} ion between the title compound and the reported YPO_4.

3.3. Thermal stability

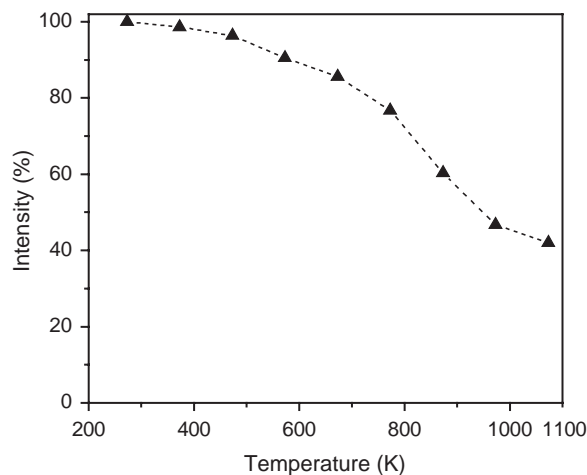Fig. 4 shows the change of luminescent intensity of the Sb^{3+}-doped $Sr_3(PO_4)_2$ crystals calcined in the temperature ranges from 373 to 1073 K for 2 h. The luminescent intensity of the as-synthesized Sb^{3+}-doped $Sr_3(PO_4)_2$ crystal was thought to be 100. The intensity of luminescence of Sb^{3+}-doped $Sr_3(PO_4)_2$ crystals decreases as the calcinations temperature increases. We consider that the decreasing intensity is due to the Sb sublimating from the crystal lattice because the emission spectrum is not changed in the calcined process monitored by XRD. It is observed that the intensity of luminescence decreases very slowly when the calcinations temperature is lower than 673 K even though it decreases rapidly when the calcinations temperature increases above 673 K. The luminescent intensity of the sample calcined at 1073 K is about 42% of the as-synthesized sample. This result shows that this compound is relatively thermally stable up to 673 K.

4. Conclusions

In this work, Sb^{3+}-doped $Sr_3(PO_4)_2$, a kind of blue phosphor material was synthesized through a milder hydrothermal method at about 513 K instead of a high temperature solid-state method at about 1400 K. The photoluminescent property of Sb^{3+}-doped $Sr_3(PO_4)_2$ crystal showed the emission band with the peak at about 396 nm. The full-width at half-maximum of the emission peak was about 65 nm and is nearly approach the reported 60 nm of aluminates blue light phosphor material. The excitation spectrum consists of a doublet band around 215 nm and a triplet band around 250 nm. The luminescent property of this compound was thermally stable up to 673 K. These results show that this compound can be a good candidate for the blue luminescent material.

Acknowledgments

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