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Phase characterization and tunable photoluminescence of Eu-doped strontium-substituted nanohalophosphate

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Abstract

Nanocrystalline Eu-doped powders, $Ca_{5-x}Sr_x(PO_4)_3(OH):Eu^{3+}$, were prepared from chemical solutions at room temperature. The crystalline phase and photoluminescence (PL) properties of the halophosphate powders were studied in terms of solution pH value and annealing atmosphere. At pH $= 2$, both $Ca_{8.3}Sr_{1.7}(PO_4)_6Cl_2$ and $Ca_{8.3}Sr_{1.7}(PO_4)_6(OH)_2$ phases were detected, but an increase in solution pH value over 7 led to the formation of only $Ca_{8.3}Sr_{1.7}(PO_4)_6(OH)_2$ phase. After annealed at 850 °C, the sample prepared in pH $= 2$ solution shows stronger blue emission than that prepared in pH $= 10$ in the reducing atmosphere. However, for the samples annealed in air atmosphere, the blue emission still can be observed that can be attributed to the reduction of $Eu^{3+} \rightarrow Eu^{2+}$. The relative intensity of blue to red emissions is dominated not only by annealing atmosphere but also by crystalline phase formed in the sample. These results indicate that the PL properties can be tunable by controlling the solution pH value (crystalline phase) and changing annealing atmosphere.

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1. Introduction

Calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; CaHAP) is a naturally occurring biomaterial. The synthesized material finds wide applications in chromatographic adsorbents, acid and base catalysts and so on [1,2] and has been used for illumination purposes and has long been known as halophosphate phosphor [3,4].

Halophosphates luminophores are characterized by the general formula $Ca_5X(PO_4)_3A,B$, where X denotes F^-, Cl^-, Br^- or OH^- ions, and A and B represent activators and sensitizers, respectively. Recently this material has been studied due to the applications in three-band fluorescent lamps and field-emission displays as well as display devices, in which the phosphor must be efficient and stable under the VUV excitation. Traditionally, these halophosphates were prepared by a solid-state reaction method and the effect of the reaction conditions on the photostimulated luminescence of polycrystalline $Sr_9Ca(PO_4)_6Cl_2$:Eu was studied. [5] Furthermore, the formation of the apatites involves the formation of various intermediates, and the preparation of luminescent-grade raw materials is critically dependent on various parameters such as pH values and precipitation temperature [6].

Recently, some techniques have been reported for the preparation of europium-activated alkaline-earth-metal chlorophosphate luminophores through solution processing. However, the effect of nanohalophosphate phosphor particle on its crystalline phase and luminescence characteristics has not been systematically investigated, especially the role of annealing atmosphere in phosphor emission. Therefore, in this work, nanohalophosphate phosphor particles synthesized from different pH-value solutions will be studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM) at ambient

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temperature. The influence of pH value in the precursor solution and annealing atmosphere on the crystalline phase, morphology and luminescence characteristics of halophosphate phosphor nanoparticles will be discussed.

2. Experimental procedure

In a typical experiment, reagent-grade $Ca(NO_3)_2$, $SrCl_2$, urea, NH_4NO_3, and europium nitrate were dissolved in 100 ml of HCl solution at pH = 1–2 and then diammonium hydrogen phosphate (DAP) was added. The molar ratio of (Ca + Sr + Eu)/P was fixed at 1.67 and the pH value of the resulting sol solution was controlled by the addition of ammonia. Then, the solid precipitate was filtered, washed with deionized water and then air-dried overnight at 60 °C. After that, the resulting white polycrystalline powder was annealed at 850 °C in reducing atmospheres, then fast cooled to ambient temperature.

The powdered samples were characterized by XRD with CuKα radiation ($\lambda = 1.5418$ Å). The morphology and microstructure of the nanoparticles were examined by (SEM JEOL-6500F). Luminescent properties are characterized by photoluminescence (PL) (FL F4500, Hitachi) measurement under the excitation of 254 nm at room temperature.

3. Results and discussion

3.1. Phase and microstructure development

Fig. 1 shows the XRD patterns of the halophosphate particles synthesized from chemical solutions with pH values of 2, 8 and 10. As shown in Fig. 1(a), both $Ca_{8.3}Sr_{1.7}(PO_4)_6Cl_2$ and $Ca_{8.3}Sr_{1.7}(PO_4)_6(OH)_2$ (HAP) phases can be observed for the samples prepared in the

solution of pH = 2. When the pH value in the solution was controlled at pH = 8, it was observed that no $Ca_{8.3}Sr_{1.7}(PO_4)_6Cl_2$ phase can be clearly detected. At a higher pH solution of 10, all the peaks of the synthesized powders are characteristic of only HAP phase and the solution shows enhanced crystallization of the HAP phase compared to that at pH = 8. Fig. 2 displays the SEM pictures of the halophosphate particles synthesized from

Fig. 2. SEM microstructure of the halophosphate particles synthesized from chemical solutions with different pH values: (a) pH = 2, (b) pH = 8, and (c) pH = 10 at room temperature.
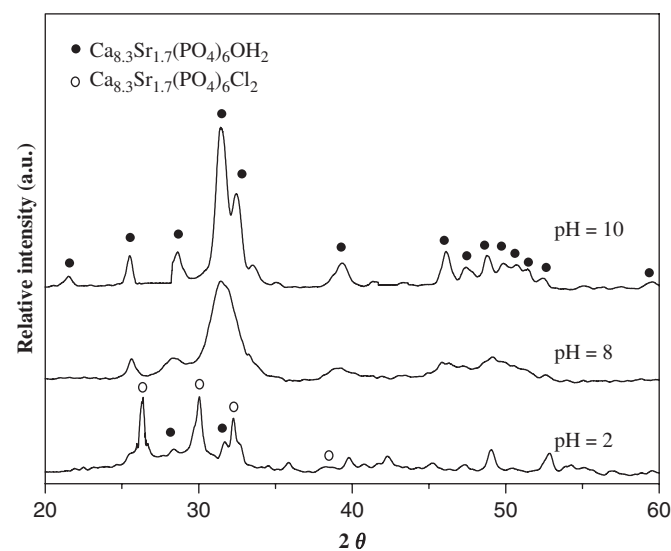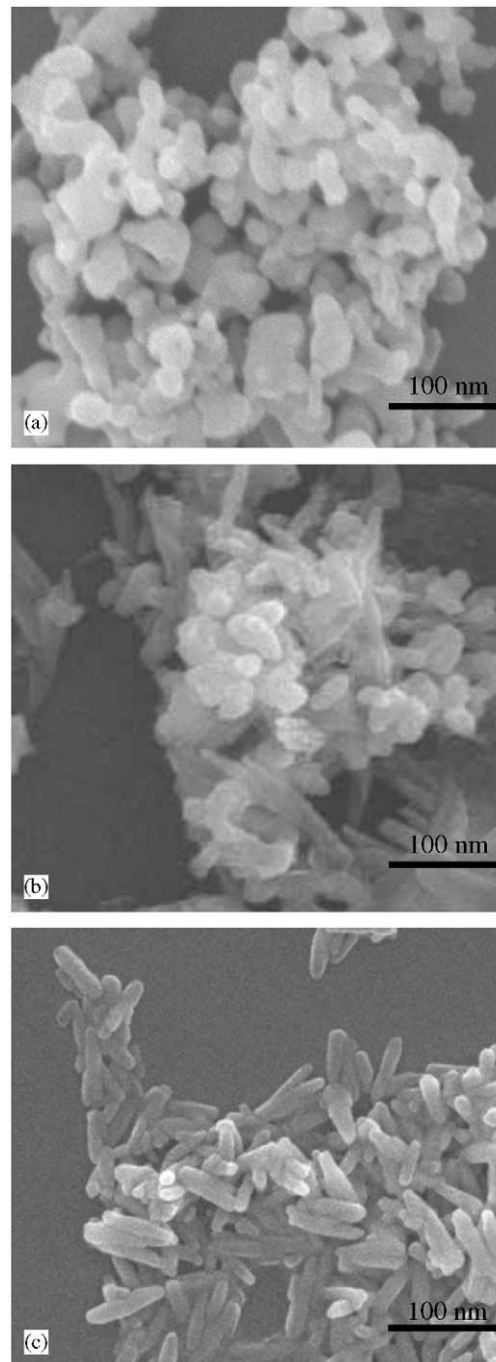

Fig. 1. X-ray diffraction patterns of nanohalophosphate synthesized from chemical solutions with different pH values at room temperature.

chemical solutions with different pH values (pH = 2, 8, and 10). All the synthesized particles with diameters are less than 100 nm, indicating that the nanohalophosphate particles can be synthesized via wet chemical process at room temperature. At pH = 2, all the particles were spherical as shown in Fig. 2(a). However, an increase in the pH value of the chemical solution causes the morphology change of halophosphate particles from spherical to rod shape as shown in Fig. 2(b) and (c). It was believed that the formation of rod-like crystals is related to the HAP structure, as evidenced from XRD patterns. The HAP particles prepared in the basic solution display the rod-like shapes but they grew spherically in the acid solution. It can be inferred, therefore, that Cl^- ions made the HAP particles grow spherically. There are several reports on the influence of Cl^- ions on the formation and structure of CaHAP particles. According to the report of Yasukawa et al. [7], the Cl^{-1} ions in the starting solution are considered to contribute to the crystal growth of these CaHAP particles. Koutsoukos et al. [8] reported that Cl^- ions altered the crystal shape of CaHAP from needles to plates. However, details of the mechanism by which Cl^- ions affect the morphology of CaHAP particles remain unclear.

As the as-precipitated powder was annealed at 850 °C in H_2/N_2 reducing atmospheres for 2 h, the XRD patterns of the halophosphate powders in Fig. 3 show that the crystallinity of both $Ca_{8.3}Sr_{1.7}(PO_4)_6Cl_2$ and HAP phases was enhanced through thermal annealing but those crystalline phases remained unchanged (i.e., HAP does not transform into β-TCP) even though those powders were annealed in different atmospheres of N_2 and air. This result indicates that those nanohalophosphate powders were thermally stable.

3.2. Eu effect

Luminescent properties of the halophosphate powders are characterized by PL measurement under 254 nm excitation. There were two broad emission bands peaked at red emission (612 nm) and blue emission (450 nm). The relative PL intensities in terms of doped-Eu^{3+} content are shown in Fig. 4 for the halophosphate powders synthesized at pH = 10 and then annealed at 850 °C for 2 h in air atmosphere. It was found that, with the addition of Eu, up to 7 mol%, the peak intensity of blue emission was decreased but red emission (612 nm) was increased. Above that, the relative emission intensity was decreased because of concentration quenching. Furthermore, at a higher temperature of 850 °C, more Eu^{3+} ions were probably incorporated into the host lattice to substitute for Ca^{2+} ions in apatite where it is usually considered that rare-earth ions occupy mainly Ca(II) sites with Cs symmetry (6h site) [9]. A charge compensation mechanism proposed by Peng et al. [10] can be used to elucidate the effect of Eu^{3+} ions substituting for Ca^{2+} ions and is described below.

When the trivalent Eu^{3+} ions were doped into $Ca_{8.3}Sr_{1.7}(PO_4)_6(OH)_2$, they replace the Ca^{2+} ions of $Ca_{8.3}Sr_{1.7}(PO_4)_6(OH)_2$. In order to keep the charge balance, two Eu^{3+} ions should be needed to substitute for three Ca^{2+} ions. Hence, one vacancy defect represented as V''_{Ca} along with two negative charges and two positive defects of Eu'_{Ca} would be created by each substitution of every two Eu^{3+} ions in the compound of $Ca_{8.3}Sr_{1.7}PO_4)_6(OH)_2$:Eu. The vacancy V''_{Ca} then acted as a donor of electrons, while the two Eu'_{Ca} defects became acceptors of the electrons. Consequently, the electrons in the vacancy defects V''_{Ca} would be transferred to Eu'_{Ca} sites and thus Eu^{3+} could be possibly reduced to Eu^{2+}. In this condition, especially at high annealing temperature, more Eu^{3+} ions would be reduced to Eu^{2+}.
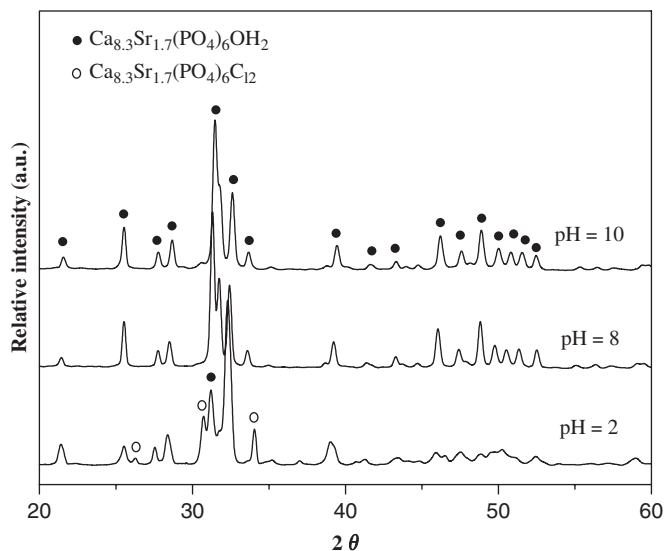

Fig. 3. XRD diffraction patterns of halophosphate powders synthesized from chemical solutions with different pH values and then annealed at 850 °C for 2 h in H_2/N_2 atmosphere.
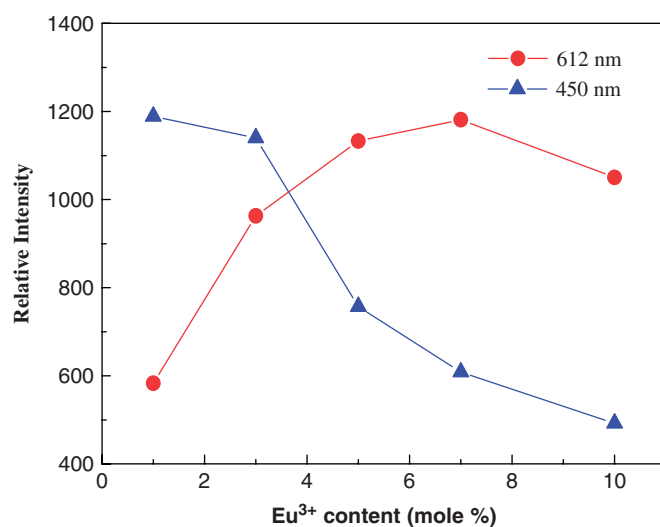

Fig. 4. Effect of doped-Eu^{3+} content on relative PL intensity of halophosphate powders prepared in a pH = 10 solution and annealed at 850 °C in air atmosphere.

3.3. Photoluminescence characterization

Fig. 5 shows the room-temperature emission (excited at 254 nm) spectra of the halophosphate powder synthesized at different pH-value solutions. In Fig. 5(a), it was found that all the as-precipitated powders only showed one Eu^{3+} red emission of $^5D_0 \rightarrow {}^7F_2$ (612 nm) independent of the solution pH value. The strongest red emission appears in the sample prepared in pH = 8 solution. This result may be attributed to the fact that the Eu ions easily react with OH^- in the pH = 8 solution to form $Eu(OH)^{2+}$ and $Eu(OH)_2^+$ [11] compared to the solutions with pH = 2 and 10.

When the synthesized powders were annealed at 850 °C in a reducing atmosphere, the PL spectra of the halophosphate powders were strongly influenced by the pH value in the chemical solution. As shown in Fig. 5(b), two emission peaks (590 and 612 nm) clearly result from the f–f transitions of the Eu^{3+} ion and the other broad peak (450 nm) should be due to Eu^{2+} emission. As can be seen, the pH = 2 powder displays the strongest Eu^{2+} emission

(450 nm) and Eu^{3+} emission (612 nm). This phenomenon is probably related to the reduction of Eu^{3+} to Eu^{2+} and the crystalline effect of the $Ca_{8.3}Sr_{1.7}(PO_4)_6Cl_2$. This may indicate that part of the Eu^{3+} ions was more easily reduced to Eu^{2+} in the $Ca_{8.3}Sr_{1.7}(PO_4)_6Cl_2$ matrix when the sample was subjected to thermal activation at 850 °C in H_2/N_2 reducing atmosphere. In addition, both $Ca_{8.3}Sr_{1.7}(PO_4)_6Cl_2$ and $Ca_{8.3}Sr_{1.7}(PO_4)_6(OH)_2$ phases formed in the pH = 2 solution make contributions to blue and red emissions, respectively. In contrast, when the samples were prepared in the pH = 10 solution, it was noted that although those samples were annealed in reducing atmosphere, a pure sharp blue emission cannot be obtained. In other words, red emission was always detected, which is attributed to the existence of $Ca_{8.3}Sr_{1.7}(PO_4)_6(OH)_2$. This reveals that the crystalline phase plays an important role in the relative intensity of blue to red emission.

Fig. 6 shows the PL spectra of the samples annealed at 850 °C in H_2/N_2 and air atmospheres for 2 h as a function of solution pH value. As shown in Fig. 6(a), stronger
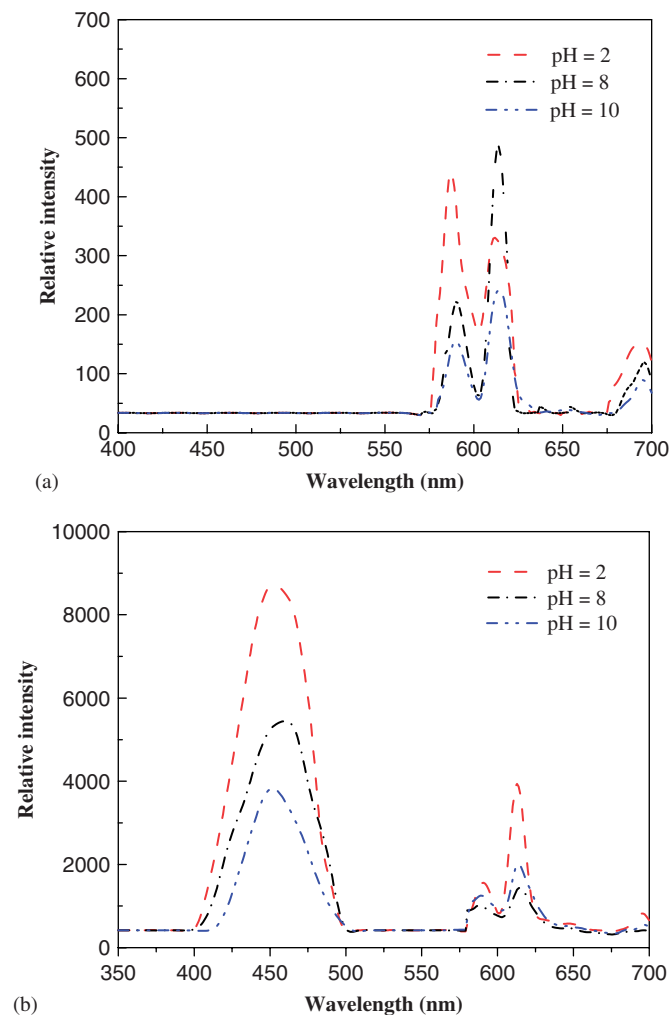

Fig. 5. PL spectra of the (a) as-precipitated and (b) annealed halophosphate powders at 850 °C in a reducing atmosphere for 2 h showing the dependence of different pH solutions.
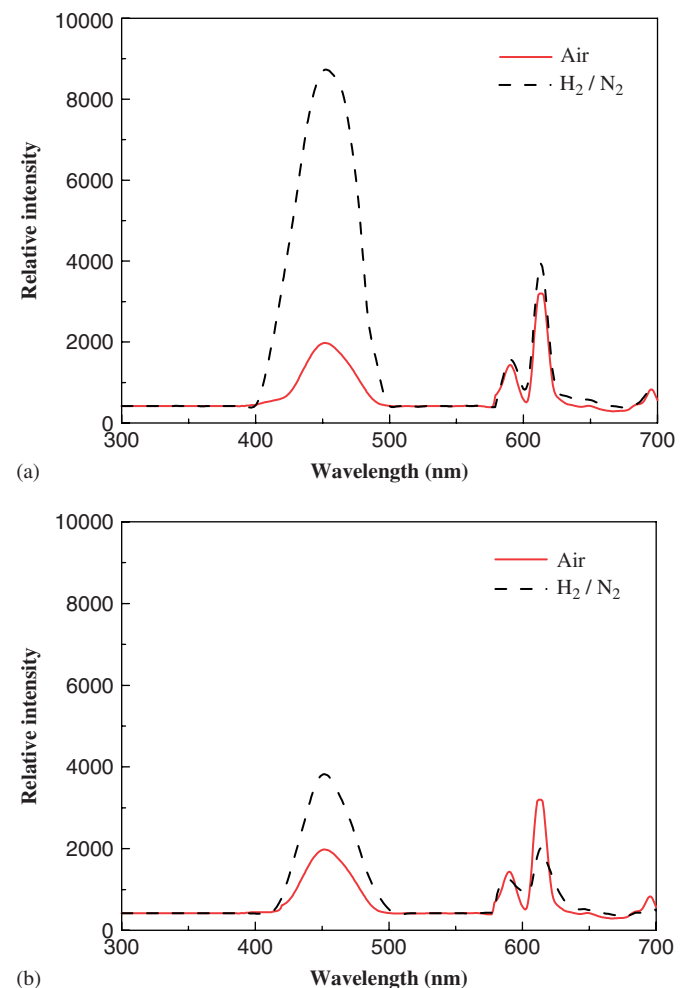

Fig. 6. PL spectra of the halophosphate powders prepared from the solution with different (a) pH = 2 and (b) pH = 10 values and then annealed at 850 °C in air and H_2/N_2 atmospheres for 2 h.

blue and red emissions were observed for the samples synthesized in pH = 2 solution and annealed in the H_2/N_2 reducing atmosphere. When the samples were annealed in air atmosphere, the blue emission became weaker as compared to that annealed in reducing atmosphere but the red emission showed little change. This reveals that the reduction of $Eu^{3+} \rightarrow Eu^{2+}$ in the sample becomes important for blue emission.

As mentioned above, when annealed at 850 °C in the H_2/N_2 reducing atmosphere, a stronger blue emission can be observed for the samples prepared in the pH = 10 solution but the observation is reversed for the sample annealed in air atmosphere as shown in Fig. 6(b). It was noted that although the sample belongs to the HAP phase (as evidenced from Fig. 3), it displays a blue emission when annealed in air atmosphere. This reveals that, in addition to reducing atmosphere, the reduction of $Eu^{3+} \rightarrow Eu^{2+}$ in the sample was also possible in air atmosphere. A similar observation was also reported by Peng et al. [12] that the reduction of $Eu^{3+} \rightarrow Eu^{2+}$ occurred in Eu-doped $Sr_4Al_{14}O_{25}$. Furthermore, a much reduced blue emission was observed for the sample prepared in pH = 10 solution (Fig. 6(b)) compared to that prepared in pH = 2 solution (Fig. 6(a)) although both samples were annealed in the same reducing atmosphere. These results indicate that the crystalline phase formed in the sample plays a more important role in PL properties than annealing atmosphere. Therefore, it is suggested that the emission from one red to blue-red can be obtained by varying the pH value of the precursor solution and controlling the annealing atmosphere.

4. Conclusion

Nanocrystalline Eu-doped halophosphate particles with diameter less than 100 nm were synthesized from chemical solutions at room temperature. The crystalline phase formed was dependent on the pH value in the solution. At pH = 2, both $Ca_{8.3}Sr_{1.7}(PO_4)_6Cl_2$ and $Ca_{8.3}Sr_{1.7}(PO_4)_6(OH)_2$ phases were detected, but with an increase of pH value over 7, only the single $Ca_{8.3}Sr_{1.7}(PO_4)_6(OH)_2$ phase was identified. This study implies that the crystalline phase in Eu-doped halophosphate plays a more important role in PL properties than annealing atmosphere. In addition, the relative peak intensity of red to blue emissions can be tunable by controlling the solution pH value (crystalline phase) and changing annealing atmosphere.

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