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Synthesis of orthorhombic and cubic PbF_2 by hydrothermal method

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Abstract Orthorhombic (α-) and cubic (β-) PbF_2 have been successfully synthesized via a simple hydrothermal process at 200 °C for 8 h using $Pb(C_2H_3O)_2$ and NH_4F as the raw reaction materials. The crystal structure, morphology, and optical properties of the as-synthesized samples were characterized by X-ray powder diffraction, scanning electron microscopy, and photoluminescence spectroscopy. XRD and SEM results show that the uniform β-PbF_2 microspheres and porous-microspheres with the average diameter about 3 and 5 μm, respectively, were synthesized assisting with citric acid and α-PbF_2 microrods and microtubes with a diameter about 15 and 10 μm, respectively, were synthesized assisting with acetic acid. The reaction conditions influencing the synthesis of these PbF_2 microstructures, such as reaction time, the amount of CTAB, and the molar ratio of F/Pb were investigated. On the basis of a series of observations, phenomenological elucidation of a mechanism for the growth of the β-PbF_2 microspheres and multispheres has been presented. Room-temperature photoluminescence measurements indicated that the as-prepared α-PbF_2 microrods exhibit a strong green emission.

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Introduction

PbX_2 (X = F, Cl, Br, and I) are known as the interesting material species, showing nonlinear optics, high ionic conductivity, self-trapping of electrons [1], photocatalysis [2], and transparency in a wide infrared region [3]. Therefore, many studies involving lead halides have centered on their basic spectroscopic properties and applications in the past decades [4–6]. Lead (II) fluoride (PbF_2) exists in two structural phases, orthorhombic α-PbF_2, and cubic β-PbF_2. In the orthorhombic structure, the lead ions are surrounded by nine halogen ions at different distances. This structure can also be thought of as a considerably distorted close packing of halogen ions with the lead ions accommodated in the same plane. In the cubic structure, each lead ion is at the centre of eight halogen ions situated at the corners of a surrounding cube, and each halogen ion has a tetrahedron of lead ions around it.

PbF_2 has a wide range of potential application in microelectronic and optoelectronic devices, and it has also been reported to have been used as a scintillator in electromagnetic calorimetry, high-energy particle detector, and solid electrolytes [7, 8]. Recently, many works have been done on the synthesis and property of PbF_2 by chemical methods at a low temperature [9–12]. The phase transition behavior of PbF_2 (α/β) has been also studied by various experimental and theoretical techniques [9, 13–17]. However, to the best of our knowledge, there have been no reports on the preparation of uniform PbF_2 microstructures by hydrothermal method at a low temperature.

In this work, a hydrothermal preparation of α-PbF_2 and β-PbF_2 microstructures were developed using $Pb(C_2H_3O)_2$ and NH_4F as sources. To study the growth mechanism of β-PbF_2 microspheres and multispheres, we systematically surveyed the growth process of β-PbF_2 by analyzing the samples at different growth stages, which made it possible to arrest the β-PbF$_2$ crystals in different stages of their growth. The effects of the amount of CTAB and the molar ratio of F/Pb on the structure and morphology of the final products were also our concern. Room-temperature photoluminescence measurements indicated that the as-prepared α-PbF$_2$ microrods had green emission.

Experimental section

Preparation of β-PbF$_2$ microspheres and porous-microspheres

All reagents were of analytical grade purity. Nonporous β-PbF$_2$ microspheres were synthesized as follows. First, 0.915 g $Pb(C_2H_3O_2)_2$ and 0.2137 g NH_4F were separately dissolved in 10 mL distilled water. Then, the two solutions were mixed under vigorous stirring, followed by introduction of 1.0 g citric acid ($C_6H_8O_7$). Finally, the amorphous precursor was transferred into the Teflon-lined stainless steel autoclave with a filling capacity of 70% and thermally treated at 200 °C for 8 h. After the system was cooled down to room temperature, the final products were washed with distilled water several times, and dried in air at room temperature. Porous β-PbF$_2$ microspheres were fabricated via the same preparation procedure of nonporous β-PbF$_2$ microspheres by adding CTAB into the solution as a cationic surfactant.

Preparation of α-PbF$_2$ microrods and microtubes

The α-PbF$_2$ microrods and microtubes were synthesized as follows: first, 2 mL acetic acid was added into 5 mL distilled water, 0.915 g $Pb(C_2H_3O_2)_2$ was dissolved in the solution, as solution A; 0.2137 g NH_4F was dissolved in 5 mL distilled water, as solution B. Then, solution B was dropped into the solution A slowly. When the reaction was finished, a white precipitate was obtained. Finally, the white amorphous precursor was transferred into the Teflon-lined autoclave and heated at 200 °C for 8 h. α-PbF$_2$ microtubes were obtained via the same procedure as α-PbF$_2$ microrods by just adding 0.4 g CTAB into the solution.

Characterization of α-PbF$_2$ and β-PbF$_2$

The phase composition of as-prepared powder samples was characterized by XRD (Model D/MAX2550 V, Rigaku Co., Tokyo, Japan) at a scanning rate of 5° min^{-1} in the 2θ range from 20° to 80°, with graphite monochromatized CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å) at 40 kV and 50 mA. Scanning electron microscopy was performed on an electron microscope (SEM, FEI Quanta 200, Netherlands). Photoluminescence spectra were measured at room temperature on a fluorescence (PL, PE LS55) spectrometer.

Results and discussion

The composition and phase purity of the as-prepared products were first analyzed by an X-ray diffraction. The XRD patterns of all the as-synthesized products are shown in Fig. 1. Figure 1a shows the final product synthesized only with the addition of 1.0 g citric acid at 200 °C for 8 h. All diffraction peaks in Fig. 1a can be perfectly indexed to the β-PbF$_2$, which are in good agreement with the literature values (JCPDS card No.06-0251). All diffraction peaks in Fig. 1b can also be perfectly indexed to the β-PbF$_2$ and product synthesized with the addition of 1.0 g citric acid and 0.4 g CTAB at 200 °C for 8 h. As the addition of citric acid replaced by acetic acid, all diffraction peaks in Fig. 1c can be indexed to the α-PbF$_2$, which are in good agreement with the literature values (JCPDS card No.41-1086). Figure 1d shows the XRD pattern of the final product synthesized with the addition of acetic acid and 0.4 g CTAB in the synthesis system at 200 °C for 8 h, all the diffraction peaks can also be perfectly indexed to the α-PbF$_2$. No peaks of any other phases are detected, indicating the high purity of all the products.

Size and morphology information of the as-prepared products are depicted in Figs. 2, 3. Figure 2a shows the final product of nonporous β-PbF$_2$ microspheres synthesized only with the addition of citric acid at 200 °C for 8 h. It can be seen that the as-prepared sample consists of large-scale uniform microspheres with the size of 2–5 μm

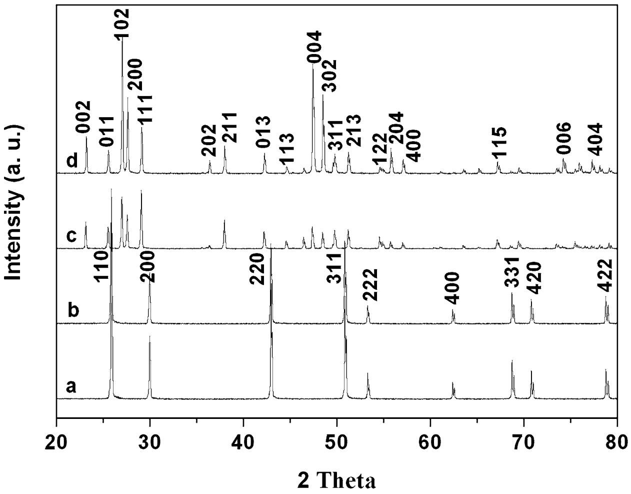

Fig. 1 XRD patterns of the final products assisted by citric acid (*a*), citric acid and CTAB (*b*), acetic acid (*c*), acetic acid and CTAB (*d*)

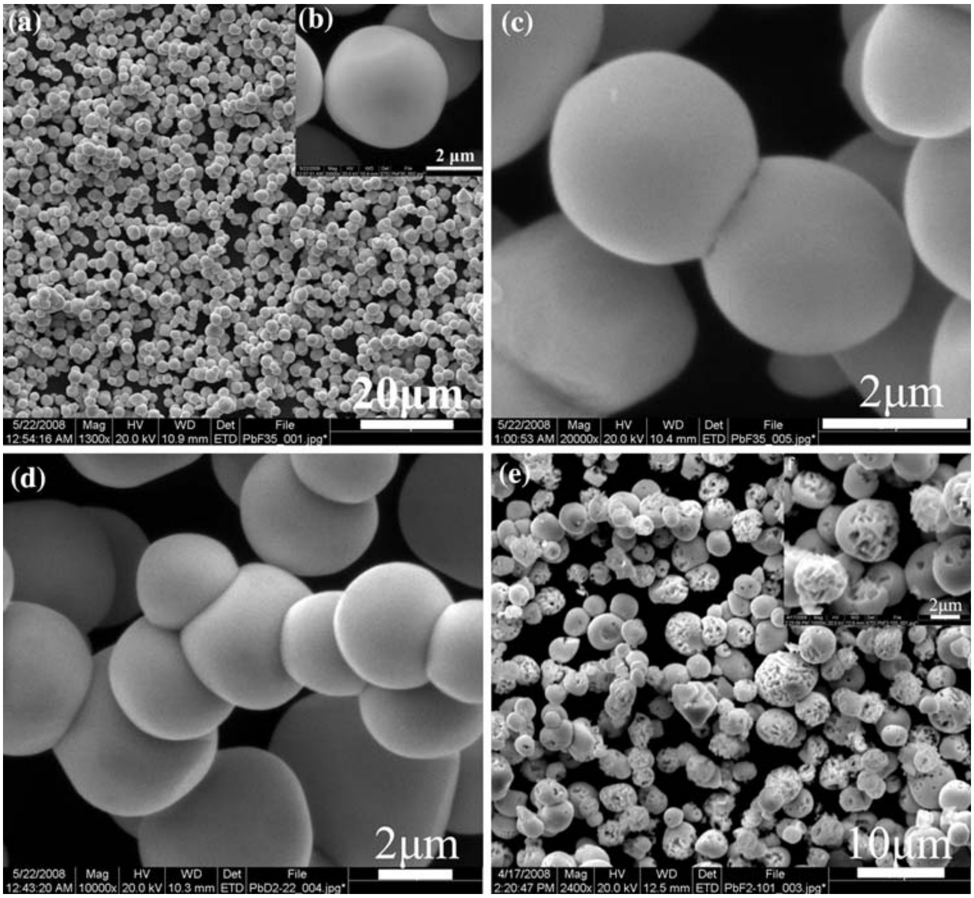

Fig. 2 SEM images of the as-prepared products assisted with citric acid (**a**), high-magnification of an isolated β-PbF_2 sphere (**b**). **c**, **d** SEM images of multispherical structures. As-prepared products assisted with citric acid and CTAB (**e**), high-magnification of β-PbF_2 porous-microsphere (**f**)

in diameter. Figure 2b represents a high-magnification SEM image of an isolated nonporous PbF_2 microsphere with a diameter of 3 μm. A twinning sphere and multi-spheres with a clear interface can also be observed in the products, as shown in Fig. 2c, d. Multispherical structures are mainly composed of more than two spheres, and each sphere has a diameter about 2–5 μm. Figure 2e shows the final product of porous β-PbF_2 microspheres synthesized with citric acid and 0.4 g CTAB at 200 °C for 8 h. It reveals that the as-synthesized products consist of large-scale porous-microspheres with the size of 2–7 μm in diameter. Figure 2f exhibits a high-magnification SEM image of porous PbF_2 microspheres. The morphology of the products assisted with acetic acid is shown in Fig. 3. Figure 3a shows the as-synthesized sample assisted only with acetic acid and it can be seen that the α-PbF_2 microrods are highly uniform with a diameter of 2–15 μm and length about 20 μm. When the final products assisted with CTAB and acetic acid, a large amount of α-PbF_2 microtubes with a diameter of 5–20 μm and length of 50–100 μm are shown in Fig. 3b. Figure 3c, d shows the high-magnification SEM images of α-PbF_2 microtubes and the tubes with a hollow tip of about 12 μm.

To understand the formation and shape evolution of nonporous β-PbF_2 microstructures synthesized only with the addition of citric acid, time-dependent experiment was conducted. The representative SEM images of the samples obtained at certain reaction time intervals are shown in Fig. 4. At the early stage of 0.5 h, the obtained white products are composed of about 300 nm nanoparticles (Fig. 4a). When the reaction time extended to 1 h, the final products of spheres with a diameter of 500–1500 nm were obtained, as shown in Fig. 4b. After the reaction time further increased to 4 h, all the nanospheres were grown into microspheres with an average diameter of about 4 μm (Fig. 4c). Many spheres contain a small sphere-like adjunction, a single incompletely developed twinning sphere as shown in Fig. 4d. With the reaction further progressing to 8 h, the microspheres and multispheres with uniform diameter were obtained as shown in Fig. 4e.

On the basis of the experimental results, a possible growth mechanism of nonporous β-PbF_2 microstructures can be simply described as follows. This is a typical dissolution–reprecipitation process that resulted in a gradual erosion and morphology transformation of the microstructures. In the formation process, time was the most

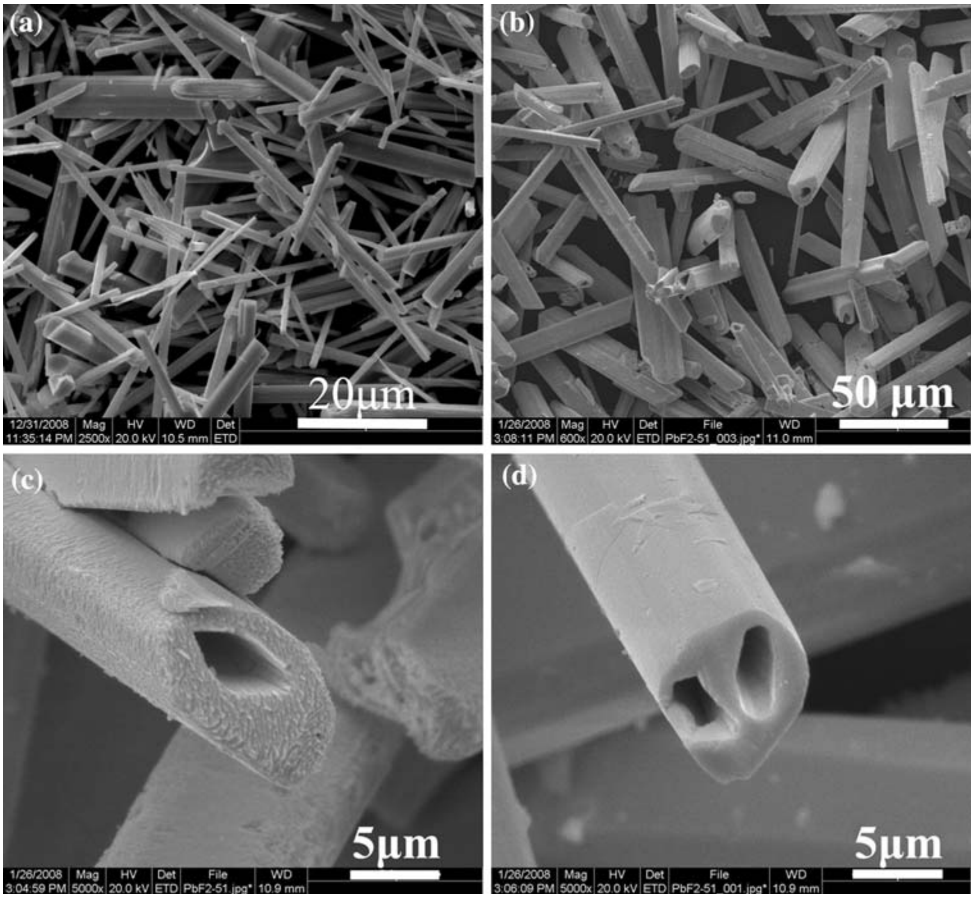

Fig. 3 SEM images of the as-prepared products assisted with acetic citric (**a**), the as-prepared products assisted with acetic citric and CTAB (**b**), high-magnification of a single α-PbF_2 microtube (**c**, **d**)

important factor controlling the size and morphology of the final products. First, there was a rapid reaction between $Pb(C_2H_3O_2)_2$ and NH_4F forming white amorphous precipitate. When sample was hydrothermally treated for 0.5 h, amorphous precipitate started crystallizing with a small sphere-like nanoparticles. With increasing the treatment time, one or more nanospheres grew bigger and the twinning or multispherical structures formed while others dissolved and reprecipitated to form relatively smooth surface of the spherical structures. In the aging time, forced by the Gibbs free energy minimization, the dissolution/reprecipitation process reoccurred until the diameters of the spheres were relatively uniform. Moreover, in this experiment, citric acid played an important role in the formation of the β-PbF_2 microstructures and multispheres. In the absence of citric acid, only α-PbF_2 could be obtained. The amounts of citric acid also affect the size and shape of the particles, and uniform spheres could be obtained with the amount of citric acid in the range from 0.5 to 2 g.

We further emphasize the importance of CTAB in the formation of well-defined porous structures. Our control experiments have shown that the amount of CTAB is crucial in the synthesis of PbF_2 porous-microspheres. By adjusting the amount of CTAB, PbF_2 with different morphologies can be obtained accordingly, and the corresponding SEM images are shown in Fig. 5a–e. In the absence of CTAB, uniform PbF_2 microspheres and multispheres were formed as shown in Fig. 5a. When an amount of 0.2 g CTAB was added into the synthesis system, uniform PbF_2 microspheres with interesting etched-pattern were obtained as shown in Fig. 5b. PbF_2 microspheres with interesting etched-pattern were shown in Fig. 5c, the diameter of the spheres without any clear changed. Further increase in the amount of CTAB to 0.4 g, porous-microspheres with a diameter in the range of 2–7 μm were shown in Fig. 5d. When an amount of 0.8 g CTAB was added into the solution, the size and shape of the final products without appearance changed as shown in Fig. 5e. As is well known, CTAB is an ionic compound, which ionizes completely in water. In the synthetic procedure of nanomaterials or microstructures, the CTAB was used as a capping agent or a "soft" template. As so far, the CTAB has been systematically studied in the synthesis of mesostructured materials and tube-like structures [18–21]. In our system, the CTAB may used as a "soft" template to synthesize PbF_2 porous-microspheres and microtubes. On the other hand, CTAB is a cationic surfactant, which could form a shell surrounding the particles to prevent PbF_2

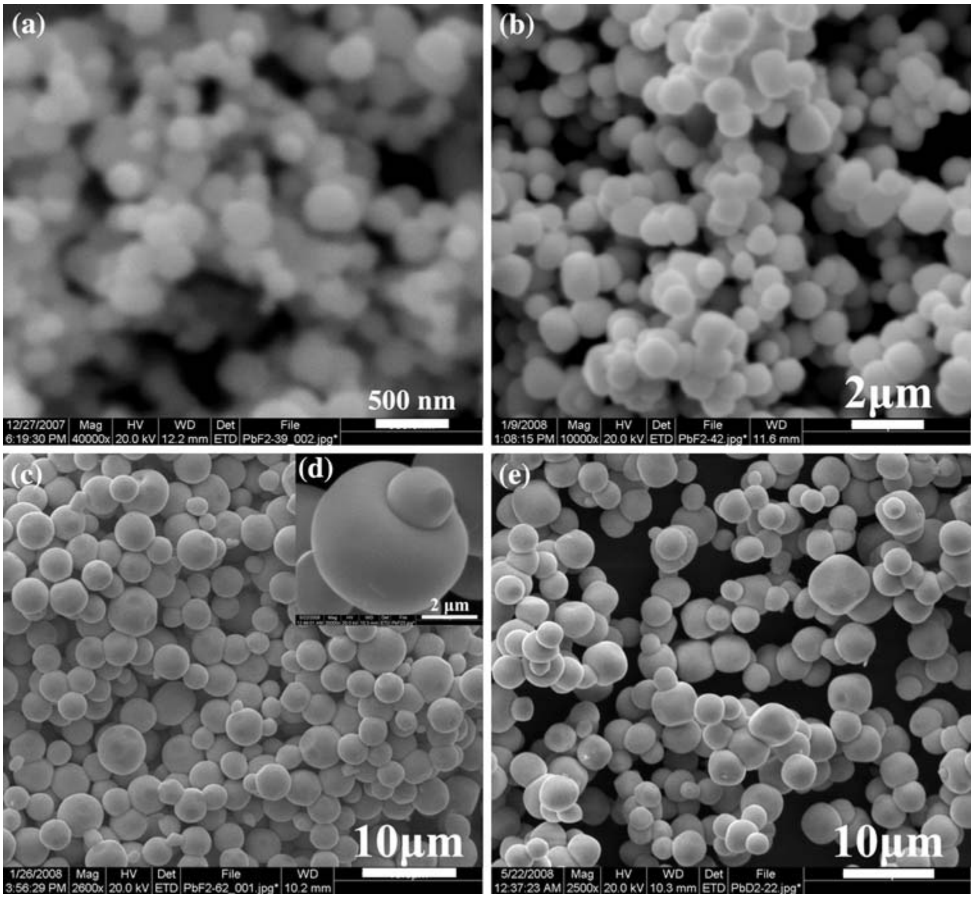

Fig. 4 SEM images of the as-prepared products for different times: **a** 0.5 h, **b** 1 h, **c**, **d** 4 h, **e** 8 h

particles from being aggregated into larger particles, so few multispheres could be found in the final products.

The kinetics of the fluoride ions driven phase transition was studied from the X-ray diffraction patterns by observing the appearance and growth of orthorhombic diffraction peaks at different molar ratio (Fig. 6). All the peaks in Fig. 6a for product synthesized with F:Pb = 4:1 can be perfectly indexed based on the crystal structure of the cubic phase β-PbF_2. No impurities have been detected. With the molar ratio of F/Pb increased to F/Pb = 6:1, the purity β-PbF_2 were also founded in the final products as shown in Fig. 6b. When the molar ratio of F/Pb increased to 8:1, the trace of α-PbF_2 could be detected in the final product (Fig. 6c). With the molar ratio of F/Pb further increased to 12:1, all the peaks in Fig. 6d for the final product can be indexed to the pure orthorhombic phase PbF_2. Figure 7 shows the corresponding SEM images of the as-synthesized samples with different molar ratio of F/Pb. Figure 7a shows the sample synthesized with F/Pb molar ratio of 6:1 and regular particles were obtained and all the particles were attached together to form a rod-like structure. When the molar ratio of F/Pb increased to 8:1, β-PbF_2 microrods can be found in the as-synthesized sample (Fig. 7b). As the molar ratio of F/Pb further increased to 12:1, only β-PbF_2 microrods can be found in the as-synthesized sample (Fig. 7c). The phase transition behavior of PbF_2 (α/β) has been studied by various experiments with high pressure and theoretical techniques [13–17]. The mechanism of $\beta \rightarrow \alpha$ phase transition of PbF_2 in this system may be qualitatively explained by the theory of Ostwald ripening (O-R) and oriented-attachment (OA) [22]. The $\beta \rightarrow \alpha$ phase transition of PbF_2 involves a dissolution–precipitation equilibrium in the system. In the presence of excess fluoride ions, on the one hand, excess fluoride ions prompt the Pb^{2+} and F^- to precipitate, on the other hand, the enhanced strength of ions increase the relative solubility of small particles and larger particles of α-PbF_2 grow preferentially. In this system, in addition to O-R, the nanoparticles can themselves act as the building blocks for crystal growth as shown in Fig. 7a. An oriented pair of nanoparticles can attach to each other, eliminating the attaching free surfaces. Finally, the high crystalline β-PbF_2 microrods were formed by dissolution–recrystallization.

Most previous optical studies on PbF_2 have been done for α-PbF_2 and β-PbF_2 nanostructures and microstructures. Xu et al. [10, 12] have synthesized single-crystalline α-PbF_2 nanorods and regular octahedrons-shape particles,

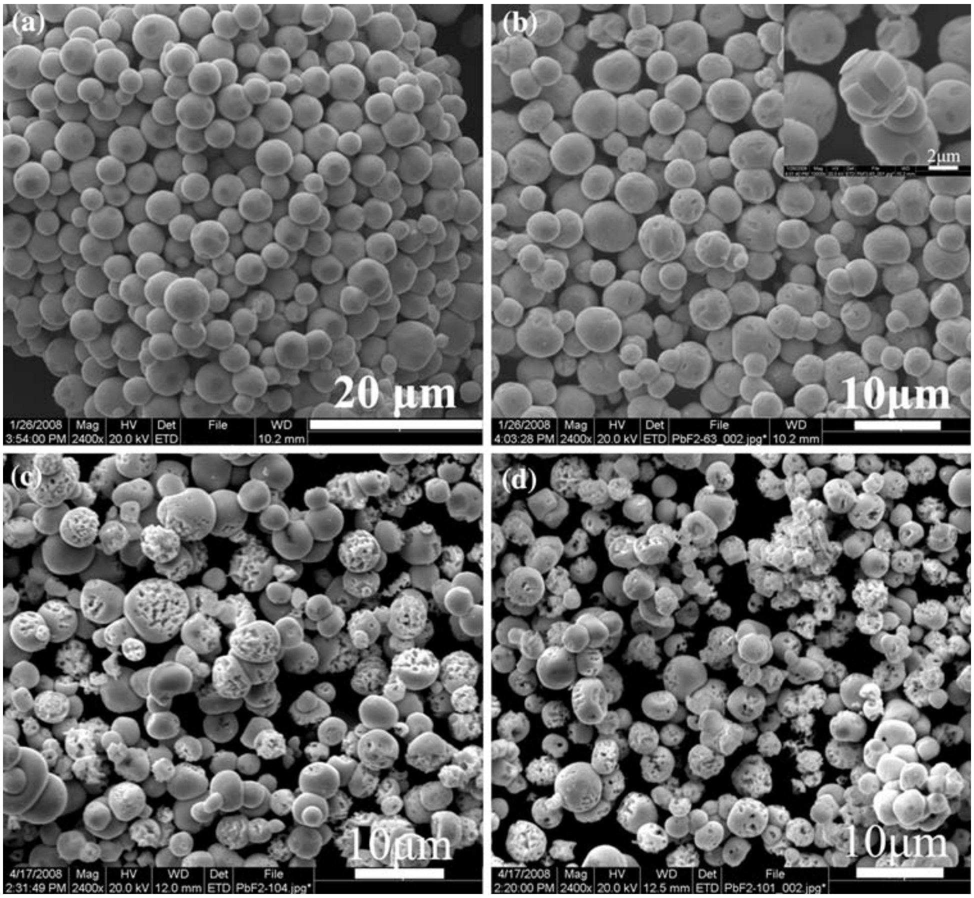

Fig. 5 SEM images of the as-prepared products of β-PbF$_2$ porous-microspheres with different amount of CTAB: **a** no CTAB; **b** 0.2 g; **c** 0.4 g; **d** 0.8 g

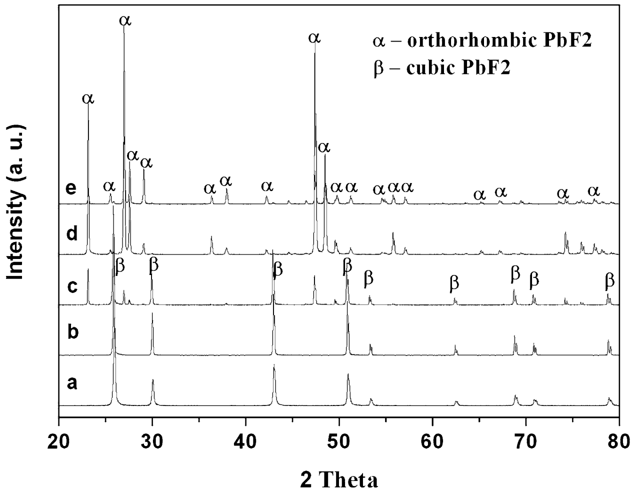

Fig. 6 XRD patterns of the final products assisted by citric acid with different ratio of F/Pb: (*a*) 4:1; (*b*) 6:1; (*c*) 8:1; (*d*) 10:1; (*e*) 12:1

which show strong green emission at room temperature. Alov and Rybchenko [16] reported the luminescence of orthorhombic bulk monocrystals of α-PbF$_2$ at low temperature of 2 K. They observed a significant quenching in luminescence as the temperature increased above 50 K, and the luminescence was almost completely quenched at about 150 K. To further characterize the α-PbF$_2$ microrods, the room temperature photoluminescence spectrum of the as-prepared sample was measured. As shown in Fig. 8, PbF$_2$ microrods give strong purple-light emission centered at 412 nm and luminescence centered at 470 nm under 325 nm excitation. To compare with previous results, the as-prepared PbF$_2$ microrods have a blue-shifted PL emission [10, 12].The PL emission may be due to the formation of electronic centre, which has similarly been observed by other researchers [23, 24].

Conclusion

In conclusion, we have synthesized orthorhombic and cubic PbF$_2$ microstructures with a simple hydrothermal method at 200 °C for 8 h using Pb(C$_2$H$_3$O)$_2$ and NH$_4$F as the raw reaction materials. Uniform β-PbF$_2$ microspheres and porous-microspheres were synthesized assisted with citric acid with average diameter of about 3 and 5 µm, respectively; α-PbF$_2$ microrods and microtubes were synthesized assisted with acetic acid with diameter of about 15 and 10 µm, respectively. A "soft" template strategy is designed to construct β-PbF$_2$ porous-spheres and α-PbF$_2$

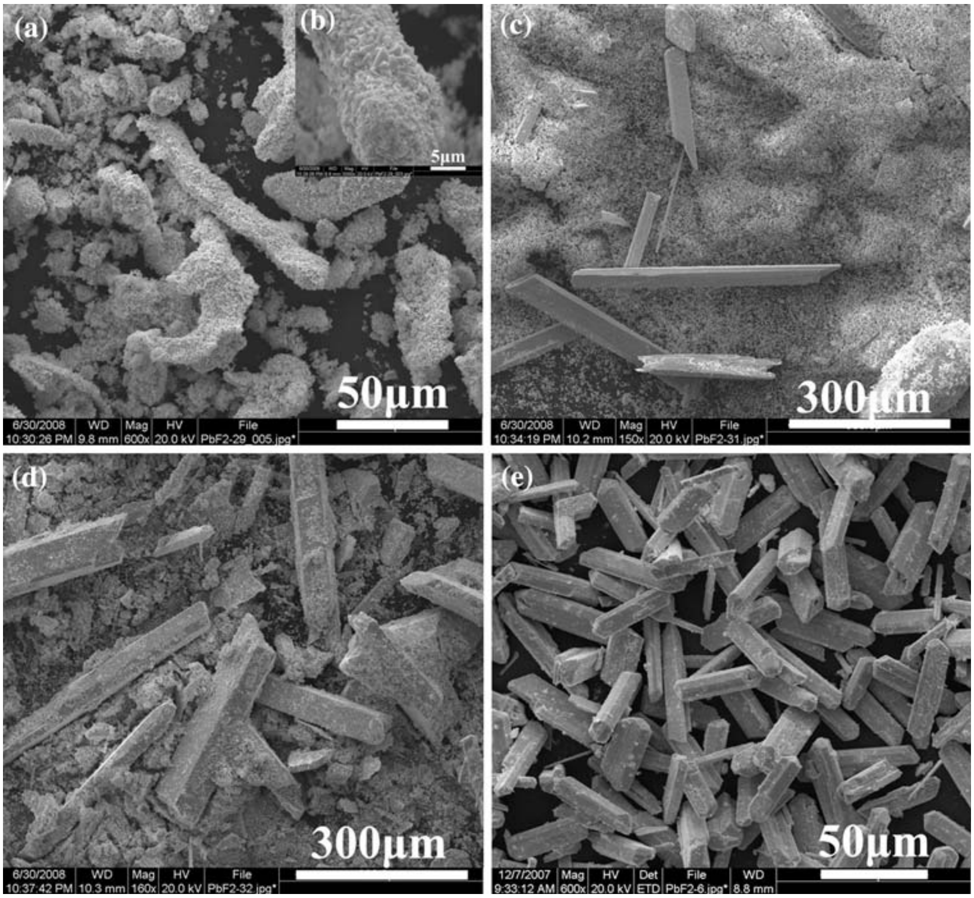

Fig. 7 SEM images of the final products assisted by citric acid with different ratio of F/Pb: **a**, **b** 6:1; **c** 8:1; **d** 10:1; **e** 12:1

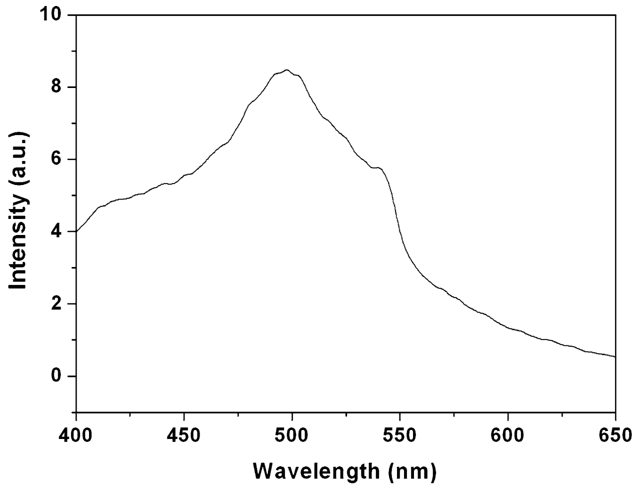

Fig. 8 PL spectra of α-PbF_2 microrods at room temperature

microtubes. Comparative investigation indicates the treatment time, the amount of CTAB, and the molar ratio of F/Pb played an important role to the shape and phase structures of PbF_2 products. Room-temperature photoluminescence measurements indicated that the as-prepared microrods had strong green emission.

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