Synthesis of PbMoO₄ nanorods by a simple sonochemical method

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Single-crystal PbMoO₄ nanorods with diameters of 70–80 nm and lengths of about 300–400 nm have been successfully obtained via a surfactant-free sonochemical method. The obtained samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and electron diffraction (ED). It is found that the precursor played a key role in the preparation of PbMoO₄ nanorods. PbMoO₄ nanorods can be successfully obtained when PbCrO₄ nanorods were used as precursor. Once PbCrO₄ were replaced with Pb(NO₃)₂, PbMoO₄ nanoparticles were formed. The synthesis mechanism was also discussed. It is rational to expect that some other one-dimensional metal molybdates may also be synthesized by this method.

Key-words : Synthesis, PbMoO₄ nanorods, Sonochemical method

1. Introduction

One-dimensional materials such as nanowires, nanorods and nanotubes have attracted considerable attention because of their unique applications in physics and fabrication of nanoscale electronic and photonic devices. Recently, PbMoO₄ has attracted great attention due to its applications in optical-instrument engineering, photoconductivity, and photoluminescence. Up to now, various techniques have been applied to synthesize PbMoO₄ crystals with different morphologies, such as hydrothermal process for PbMoO₄ microcrystals and micro-octahedrons, molten salt method and hydrothermal route for PbMoO₄ dendrites, solvothermal process, sonochemical method and microwave irradiation process for PbMoO₄ nanoparticles.

Now, it is still a challenging issue for material researchers to synthesize one-dimensional PbMoO₄ crystals, and there are few reports dealt with the preparation of PbMoO₄ with one-dimensional nanostructures. In this paper, we report for the first time the preparation of PbMoO₄ nanorods by a simple sonochemical process.

2. Experimental

All the chemicals were analytical grade purity. In a typical experiment, PbCrO₄ precursor was first prepared. 0.002 mol Na₂CrO₄ and 0.01 mol Pb(NO₃)₂ were separately dissolved in 20 ml distilled water to form aqueous solutions. Then, Pb(NO₃)₂ solution was added to Na₂CrO₄ solution under ultrasound irradiation for 0.5 h. The temperature of the solution was continuously kept the room temperature 25°C during the ultrasound irradiation. Then, the resultant precipitates were centrifuged, washed with distilled water, and dried naturally for characterization. The effect of precursor on the formation of PbMoO₄ was investigated.

The effect of precursor on the formation of PbMoO₄ was investigated. In another typical experiment, PbCrO₄ was replaced by Pb(NO₃)₂. 0.002 mol Na₂MoO₄ and 0.002 mol Pb(NO₃)₂ were separately dissolved in 20 ml distilled water to form aqueous solutions. Then, Pb(NO₃)₂ solution was added to Na₂MoO₄ solution under ultrasound irradiation for some time at 25°C. Finally, the resultant precipitates were centrifuged, washed with distilled water, and dried naturally for characterization. The effect of ultrasonic irradiation on the formation of PbMoO₄ was also investigated, and PbMoO₄ samples were prepared using PbCrO₄ and Na₂MoO₄ as precursors at the same temperature 25°C without ultrasonic irradiation.

X-ray diffraction was performed on an X-ray diffractometer (D8 Focus, Germany) using Cu Kα radiation. Transmission electron microscope (TEM) images were taken with a JEOL, 200CX TEM by using an acceleration voltage of 160 kV. The samples used for TEM observations were prepared by dispersing some powder products in ethanol followed by ultrasonic vibrations for 10 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon.

3. Results and discussion

Figures 1(a)–1(e) shows the XRD patterns of the as-prepared PbCrO₄ and PbMoO₄ samples synthesized by the sonochemical process. All of the diffraction peaks in Fig. 1(a) can be indexed to the pure monoclinic phase [space group : P2₁/n (14)] of PbCrO₄ with lattice constants a = 7.12 Å, b = 7.43 Å, c = 6.79 Å and β = 102.42°, which are in good agreement with the literature values (JCPDS No.73-2059). Figures 1(b)–1(d) shows the XRD patterns of the as-prepared PbMoO₄ samples prepared by the sonochemical process using PbCrO₄ and Na₂MoO₄ as precursors.

As displayed in Fig. 1(b), crystallized PbMoO₄ has been formed in the case of the ultrasonic time 2 min, suggesting that PbMoO₄ is easy to be crystallized. In addition, the weak diffraction peaks of PbCrO₄ were also detected, indicating that small quantities of PbCrO₄ were also detected, indicating that small quantities of PbMoO₄ nanoparticles were formed. The synthesis mechanism was also discussed. It is rational to expect that some other one-dimensional metal molybdates may also be synthesized by this method.
When the obtained PbCrO₄ nanorods were used as precursors, PbMoO₄ nanorods with rough faces were obtained. Of nanorods with length ca. 1.5 μm, as exhibited in Fig. 3(a). Obviously, the length of the PbMoO₄ nanorods became shorter and the diameter became a bit bigger compared with that of PbCrO₄ nanorods. As the ultrasonic time was further increased to 1 h, combined with the above XRD results [Fig. 1(d)], the obtained pure PbMoO₄ powders were composed of homogeneous nanorods with diameters of 70–80 nm and lengths of about 300–400 nm, as illustrated in Fig. 4(d). The corresponding electron diffraction pattern taken from a randomly chosen single nanorod is shown in Fig. 4(e), which confirms that the as-prepared PbMoO₄ nanorods are single-crystalline in structure. When the precursor PbCrO₄ was replaced with Pb(NO₃)₂, as depicted in Fig. 4(f), PbMoO₄ nanoparticles with the mean particle size of ca. 30 nm were formed, which is similar to the report.¹¹

Figure 4 shows the transmission electron microscope images of the as-prepared PbCrO₄ and PbMoO₄ samples prepared by the sonochemical method. As displayed in Fig. 4(a), the obtained PbCrO₄ were composed of nanorods with length ranging from 1 to 1.5 μm. It is clear that the obtained PbCrO₄ nanorods are quite smooth and straight along its entire length and have a relatively narrow diameter distribution ranging from 30 to 50 nm. Figure 4(b) illustrates the TEM image of the obtained PbMoO₄ samples using the as-synthesized PbCrO₄ nanorods as precursor by the sonochemical method for the ultrasonic time 2 min. It is interesting to find that the as-prepared PbMoO₄ consisted of nanorods with average diameters of ca. 50–60 nm and lengths of about 400–600 nm. Obviously, the length of the PbMoO₄ nanorods became shorter and the diameter became a bit bigger compared with that of PbCrO₄ nanorods. As the ultrasonic time was increased from 2 to 30 min, as depicted in Fig. 4(c), PbMoO₄ nanorods were also obtained. When the ultrasonic time was further increased to 1 h, combined with the above XRD results [Fig. 1(d)], the obtained pure PbMoO₄ powders were composed of homogeneous nanorods with diameters of 70–80 nm and lengths of about 300–400 nm, as illustrated in Fig. 4(d). The corresponding electron diffraction pattern taken from a randomly chosen single nanorod is shown in Fig. 4(e), which confirms that the as-prepared PbMoO₄ nanorods are single-crystalline in structure. When the precursor PbCrO₄ was replaced with Pb(NO₃)₂, as depicted in Fig. 4(f), PbMoO₄ nanoparticles with the mean particle size of ca. 30 nm were formed, which is similar to the report.¹¹

As shown in Fig. 4(f), PbMoO₄ nanoparticles were obtained based on the following reaction. Because PbCrO₄ nanorods have been successfully synthesized, we attempt to prepare PbMoO₄ nanorods using PbCrO₄ nanorods as precursors. As displayed in Figs. 4(d) and 4(e), it is interesting to find that single-crystal PbMoO₄ nanoparticles were successfully obtained. The formation of PbMoO₄ nanorods may be based on the following reaction, in which CrO₄²⁻ anions were replaced with MoO₄²⁻ anions. Furthermore, due to the larger radius of MoO₄²⁻ anions compared with that of CrO₄²⁻ anions, the diameter of the obtained PbMoO₄ nanorods became a bit larger. In addition, because the

PbCrO₄ still existed. As the ultrasonic time was increased to 30 min, as shown in Fig. 1(c), unreacted PbCrO₄ still existed. When the ultrasonic time was further increased to 60 min, as illustrated in Fig. 1(d), all of the diffraction peaks can be indexed to a tetragonal structure of PbMoO₄ with lattice constants a = 5.433 Å, c = 12.11 Å, well consistent with the literature values (JCPDS No. 74-1075). And no diffraction peaks of PbCrO₄ were found, indicating that the precursor PbCrO₄ was completely consumed. Moreover, as illustrated in Fig. 1(e), when the precursor PbCrO₄ was replaced with Pb(NO₃)₂, pure PbMoO₄ can be obtained. But, the intensity of the corresponding diffraction peaks became weaker, implying the weak crystallization of the obtained PbMoO₄ crystals.

To study the effect of ultrasonic irradiation on the formation of PbMoO₄ crystals, comparison experiments were carried out using PbCrO₄ and Na₂MoO₄ as precursors without ultrasonication and other reaction conditions were unchanged. Well-crystallized PbCrO₄ crystals still could be obtained without ultrasonication [Fig. 2(a)]. However, as displayed in Figs. 2(b)–2(d), although PbMoO₄ crystals were formed, it was still accompanied by small quantities of PbCrO₄ when the reaction time was increased from 2 to 60 min. Compared with the XRD results from Figs. 1(b)–1(d), it can be concluded that the ultrasonic irradiation was an important factor which can promote the phase transition from PbCrO₄ to PbMoO₄.

Figure 3 displays the transmission electron microscope images of the as-prepared PbCrO₄ and PbMoO₄ samples prepared using Na₂MoO₄ and the as-prepared PbCrO₄ as precursors without ultrasonication. It is found that the resulting PbCrO₄ consisted of nanorods with length ca. 1–1.5 μm, as exhibited in Fig. 3(a). When the obtained PbCrO₄ nanorods were used as precursors and the reaction time was as short as 2 min, as depicted in Fig. 3(b), PbMoO₄ nanorods were formed and a small quantity of PbCrO₄ nanorods with smooth faces were present, which was consistent with the above XRD results. When the reaction time was increased to 30 min and 1 h, as shown in Figs. 3(c)–3(d), PbMoO₄ nanorods with rough faces were obtained.
Fig. 3. TEM images of the as-prepared (a) PbCrO$_4$ samples synthesized without ultrasonication, and PbMoO$_4$ samples prepared using PbCrO$_4$ and Na$_2$MoO$_4$ as precursors without ultrasonication for different reaction times (b) 2 min, (c) 30 min and (d) 1 h, respectively.

Fig. 4. TEM images of the as-prepared (a) PbCrO$_4$ samples synthesized by the sonochemical process, and PbMoO$_4$ samples synthesized by the sonochemical process using PbCrO$_4$ and Na$_2$MoO$_4$ as precursor for the ultrasonic time (b) 2 min, (c) 30 min and (d) 1 h, respectively, (e) PbMoO$_4$ samples synthesized by the sonochemical process using Pb(NO$_3$)$_2$ and Na$_2$MoO$_4$ as precursors for the ultrasonic time 1 h. (f) PbMoO$_4$ samples synthesized by the sonochemical process using Pb(NO$_3$)$_2$ and Na$_2$MoO$_4$ as precursor for the ultrasonic time 1 h.
rearrangements of the anions and cations were performed during the formation process, the nanorods were inevitably fractured and the length of the obtained PbMoO$_4$ nanorods became shorter. Therefore, we consider that the PbCrO$_4$ nanorods played a crucial role in the formation of PbMoO$_4$ nanorods and acted as templates. The templates not only controlled the morphology of the products, but also acted as reactants. In addition, the different XRD results from Figs. 1 and 2 suggested that the ultrasonic irradiation was another crucial factor which was favorable for the phase transition from PbCrO$_4$ to PbMoO$_4$.

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\text{Pb}^{2+} + \text{MoO}_4^{2-} \rightarrow \text{PbMoO}_4 \\
\text{PbCrO}_4 + \text{MoO}_4^{2-} \rightarrow \text{PbMoO}_4 + \text{CrO}_4^{2-}
\]

4. Conclusions

Single-crystal PbMoO$_4$ nanorods have been successfully synthesized by the sonochemical method without any surfactants at room temperature. It is found that the precursor played a crucial role in the formation of PbMoO$_4$ nanorods. It could be expected that the novel and effective technique presented in this article would be extended to synthesize other one-dimensional scheelite-structured compounds. PbWO$_4$ nanorods have also been successfully synthesized by this simple process, which will be reported in the near future.

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