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Short communication

Synthesis of $BaMoO_4$ high photoluminescent whiskers by an electrochemical method

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Abstract

$BaMoO_4$ whiskers were successfully prepared by an electrochemical method. The as-prepared samples were characterized by X-ray diffraction, scanning electron microscopy and photoluminescence (PL) spectra techniques, respectively. The results showed that the samples obtained under different electric current values have little difference in crystallinity and morphology, which results in similar photoluminescence. However, when ethanol was introduced into the electrolytic solution, the aspect ratio of $BaMoO_4$ crystallites remarkably increased and their particle size decreased, exhibiting enhanced PL intensity.

Keywords: B. Whiskers; $BaMoO_4$; Photoluminescence; Electrochemical synthesis

1. Introduction

The properties of inorganic crystallites depend intimately on their microstructure, particle size and morphology, and size distribution besides chemical/phase composition. Controlling the micro-architecture and morphology of materials at all dimensions from the nanoscale to microscale is a challenging issue to material scientists [1–7]. Specifically, the research on low dimensions (1D or 2D) of inorganic nano-/micro-crystallites has increasingly attracted a lot of interests due to their fundamental importance in understanding particle size-/shape-dependent properties and their potential applications [8–12].

$BaMoO_4$ with Scheelite-type structure is one of the most important members among the metal molybdate family, which has found wide applications from photoluminescence to electro-optic fields [13–17]. Various methods have been explored to synthesize these materials, including solid-state reaction [18], electrochemical method [19,20], combustion synthesis [21], reverse-microemulsion process [22], complex polymerization [23,24], solvothermal synthesis [25,26], molten salt route [27], and microwave-assisted citrate complex method [14].

In this work, a new electrochemical method was proposed to synthesize homogeneous $BaMoO_4$ whiskers with good photoluminescence. Moreover, the morphology of $BaMoO_4$ crystallites can be controlled by adjusting processing parameters. The results show that smaller particle size and higher aspect ratio would favor enhanced PL intensity of $BaMoO_4$ crystallites. This method has obvious advantages like simple experimental set-up, easy manipulation, short reaction time, and environmental friendliness. To the best of our knowledge, no such studies have ever been reported.

2. Experimental

Barium acetate ($(CH_3COO)_2Ba{\cdot}H_2O$, ≥99.0%) was used as an electrolyte. A typical electrolytic solution was made up by 150 ml deionized water and 0.015 mol $(CH_3COO)_2Ba{\cdot}H_2O$. Two pieces of Molybdenum (Mo, >99.9%) electrode 100 mm × 20 mm × 0.5 mm in size were parallelly fixed by a Teflon holder with a interval distance of 20 mm, and were put into the electrolytic solution with a 30 mm depth of immersion. When they were connected with a DC power supply (Sunpower, U-300v, 5 A) at room temperature, the electrochemical process could be performed at different electric current values. The solvent composition of the electrolytic solution can also be tuned

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by adding ethanol (CH_3CH_2OH, ≥99.7%) into deionized water. Through varying the volume ratio of ethanol to total solvent, a series of electrolytic solutions with different ethanol loadings (20 vol.%, 40 vol.%, and 60 vol.%) were obtained, having the same $(CH_3COO)_2Ba{\cdot}H_2O$ content (0.015 mol). The whole electrochemical reaction took 10 min; after that, the precipitate was filtered and washed with deionized water and ethanol for several times, and finally dried at 60 °C in air for 6 h.

The phase composition of the as-prepared samples were detected by an X-ray powder diffraction (XRD, D/MAX—RB, Rigaku, Japan), using Cu Kα radiation (λ = 1.5406 Å) in a 2θ range from 20° to 70°. A scanning electron microscope (SEM, S-4800, HITACHI, Japan) was used for observing their particle size and morphology. The room temperature photoluminescent spectra were recorded on a spectrofluorometer (PL, Fluorolog-Tau-3, ISA, USA).

3. Results and discussion

Fig. 1 shows XRD patterns of the as-prepared samples by using different electric currents. All XRD patterns (Fig. 1(a)–(c)) can be assigned to a tetragonal phase $BaMoO_4$ with Scheelite-type structure, in a good agreement with the reported data (JCPDS: 29-0193). It means that the tetragonal phase $BaMoO_4$ can be easily prepared by this approach in the aqueous electrolytic solution of $(CH_3COO)Ba{\cdot}H_2O$. Moreover, the intensity of some XRD peaks slightly increases with an increase of the electric current value, especially of (1 1 2), (2 0 0), and (3 1 2) planes, indicating that higher electric current value would possibly promote some preferred orientation growth of $BaMoO_4$ crystallites to a certain extent.

Fig. 2 presents the effect of added ethanol on the crystallization of $BaMoO_4$ crystallites. At $I = 2$ A, with the increase of ethanol in the electrolytic solution, their XRD peak intensity remarkably weakens (Fig. 2(a)–(c)) even though all three XRD patterns can be indexed to the tetragonal $BaMoO_4$ phase. Compared with the influence of electric current, the variation of ethanol loading shows a much stronger effect on the crystallization of $BaMoO_4$ phase, especially on orientation growth. (2 0 0) and (3 1 2) peaks remarkably decline in intensity with an increase of ethanol concentration in the electrolytic solution.

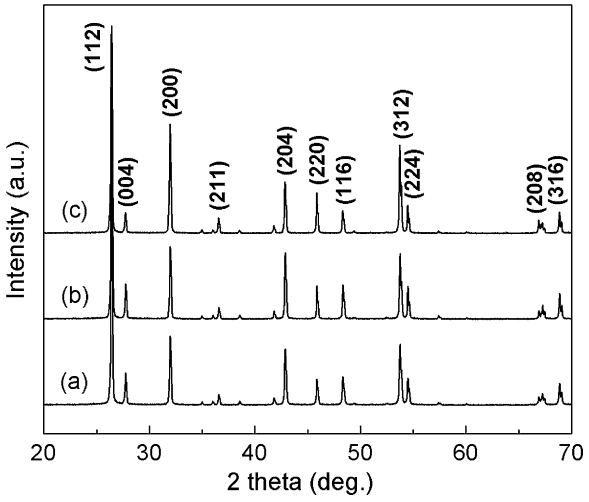

Fig. 1. XRD patterns of samples prepared at different electric current values: (a) 2 A; (b) 3 A; and (C) 4 A (without adding ethanol in the electrolytic solution).

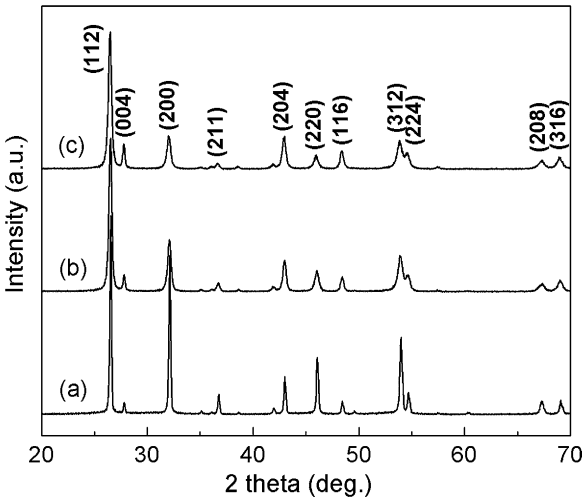

Fig. 2. Effect of ethanol loadings on the crystallization of $BaMoO_4$ phase: (a) 20 vol.%; (b) 40 vol.%; and (c) 60 vol.% ($I = 2$ A).

Fig. 3 gives SEM images of above samples. The samples obtained without adding ethanol (Fig. 3(a)–(c)) have similar particle morphology and consist of shuttle-like as well as flower-shaped crystallites. The amount of shuttle-like $BaMoO_4$ crystallites showing preferred orientation growth progressively increases with the increase of electric current value, which is well consistent with the XRD analysis results in Fig. 1. Fig. 3(d)–(f) clearly illustrates an evolution process of $BaMoO_4$ crystallites morphology with the increase of ethanol in the electrolytic solution. Evidently, the addition of ethanol would not only favor the preferred orientation growth of $BaMoO_4$ crystallites to result in a high aspect ratio, but also reduce their particle size. At 60 vol.%, homogenous and well-dispersed whiskers can be successfully obtained. Meanwhile, if controlled appropriately, the morphology of $BaMoO_4$ crystallites can be tuned only by varying ethanol loadings from shuttle-like shape (Fig. 3(d)) to microrods (Fig. 3(e)), and whiskers (Fig. 3(f)).

The mechanism for forming $BaMoO_4$ crystallites in the electrolytic solution can be described as follows:

$$Mo + 4H_2O \rightarrow MoO_4^{2-} + 8H^+ + 6e^- \quad (1)$$

$$MoO_4^{2-} + Ba^{2+} \rightarrow BaMoO_4 \downarrow \quad (2)$$

When a given electric potential was applied on Mo electrodes, an electrochemical process would proceed. As shown in Eq. (1), metal Mo would oxidize to form MoO_4^{2-}, which could further combine with Ba^{2+} in the electrolytic solution to produce $BaMoO_4$ precipitation when its solubility product was reached. In addition, the change in chemical constituent of the electrolytic solution also had a great influence on the particle size and morphology of $BaMoO_4$ crystallites.

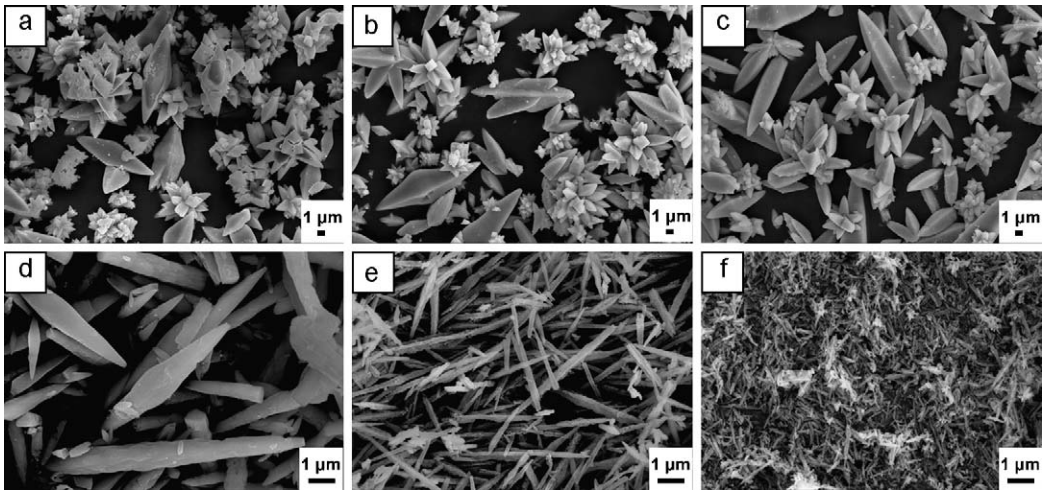

Fig. 3. SEM images of $BaMoO_4$ crystallites prepared under different electrochemical conditions: (a) 2 A, (b) 3 A, and (C) 4 A (without adding ethanol); adding (d) 20 vol.%, (e) 40 vol.%, and (f) 60 vol.% ethanol in the electrolytic solution ($I = 2$ A).

Compared with the electrolytic solution without adding ethanol, the mixture of ethanol and water as a mixed solvent would reduce the dielectric constant of the electrolytic solution since the dielectric constant of ethanol (24 at 25 °C) is smaller than that of water (78 at 25 °C). Thus, the solubility product of $BaMoO_4$ precipitate can be more easily reached due to its decreased solubility [28], which results in the formation of more nuclei and smaller crystallite size. Meanwhile, since there it is possible the selective absorption of ethanol to occur on the crystallographic plane [29], it will change the growth rate of $BaMoO_4$ crystallographic plane with different surface energy and finally lead to the preferred orientation growth.

The PL of the as-synthesized products was also investigated at room temperature with 350 nm excitation wavelength. As shown in Fig 4(a)–(c), on the absence of ethanol, the $BaMoO_4$ samples exhibit the lowest PL intensity, and the variation of electric current from 2 A to 3 A, 4 A does not cause any significant difference in their PL spectra. It should be attributed to the similarity in their particle size and morphology (Fig. 3(a)–(c)). However, once ethanol was introduced in the electrolytic solution, at the same electric current ($I = 2$ A), this organic solvent would greatly enhance PL intensity of $BaMoO_4$ crystallites (Fig. 4(d)–(f)). At 60 vol.%, the highest PL intensity can be obtained. Combining with SEM observation in Fig. 3, it can be concluded that small particle size and high aspect ratio would be beneficial to the improvement of $BaMoO_4$ PL photoluminescence. Similar results can be also found in the literature [30,31].

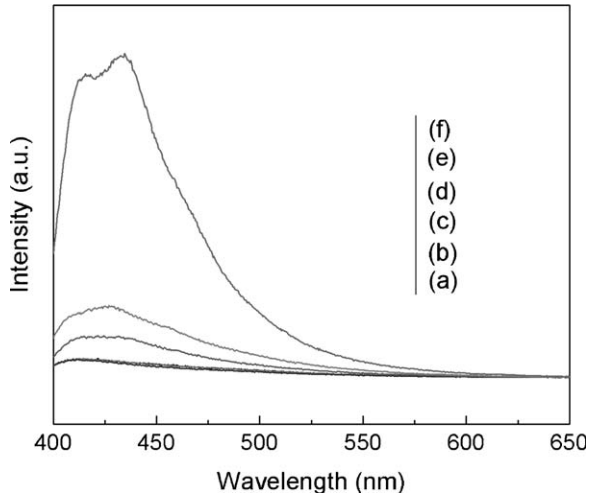

Fig. 4. Photoluminescent spectra of $BaMoO_4$ crystallites prepared under different electrochemical conditions: without adding ethanol, (a) 2 A, (b) 3 A, and (C) 4 A; and at $I = 2$ A, adding (d) 20 vol.%, (e) 40 vol.%, and (f) 60 vol.% ethanol in the electrolytic solution, respectively.

4. Conclusions

Tetragonal $BaMoO_4$ crystallites with different particle size and morphology can be easily prepared at room temperature by a simple and rapid electrochemical route. In comparison with the electric current factor, the ethanol content in the electrolytic solution shows a stronger influence upon the crystallization of $BaMoO_4$, especially on preferred orientation growth. Increasing ethanol would reduce the particle size of $BaMoO_4$ crystallites and increase their aspect ratio, finally enhancing PL intensity. At $I = 2$ A, homogeneous and well dispersed $BaMoO_4$ whiskers with the strongest PL intensity can be obtained in the electrolytic solution containing 60 vol.% ethanol.

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