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Controllable route to barium molybdate crystal and their photoluminescence

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ABSTRACT

A simple precipitation route has been developed to synthesize $BaMoO_4$ with different morphologies, such as flower-like spheres, spindle-like and octahedron crystals, by using a novel organic compounds poly-(styrene-alt-maleic acid) (PSMA) as crystal growth modifier. The concentrations of PSMA and reactants have significant influences on the morphology control of $BaMoO_4$. PSMA efficiently controls the morphology by inhibiting the oriented growth direction. The photoluminescence spectra show broad green emission at 530 nm, which is attributed to the $^1T_2 \rightarrow {}^1A_1$ transition in the intrinsic MoO_4^{2-} group.

1. Introduction

In the past few years, intensive efforts have been devoted to the controllable synthetic method of crystals, since the morphology, size, structure and dimensionality of crystals have great impacts on their physical, chemical and other intrinsic properties [1–28]. Among various synthesis methods, biomineralization method assisted by some special organics has been widely used to synthesize crystals with controllable morphology and size [29,30]. A series of inorganic compounds including $CaCO_3$ [31–33], $BaSO_4$ [34,35], $BaCO_3$ [36,37] etc., have been successfully synthesized using effective polymers to control the nucleation and crystal growth of the as-prepared inorganic compounds. As one of the important materials in the electro-optical industry, $BaMoO_4$ attracts great attention due to its promising applications in solid-state lasers [38], photocatalysts [39] and photoluminescence emission (PL) [40]. Currently, several methods have been developed to prepare $BaMoO_4$, such as microwave-assisted synthesis [41,42], hydrothermal route [43], microemulsion route [44], complex polymerization method [45] and electrochemical method [46]. However, biomineralization route to $BaMoO_4$ has been rarely reported to date [47]. In this work, $BaMoO_4$ crystals with distinct morphologies were fabricated via a biomineralization route, by using the poly-(styrene-alt-maleic acid) (PSMA) as crystal growth modifier at room temperature. The morphology evolution of crystals is investigated through adjusting concentrations of both PSMA and reactants. Room temperature photoluminescence (PL) spectra show that the optical properties could be modulated by different morphologies. The biomineralization method is proved to be convenient, economical, practical and environmental, which may provide new insights on the controllable synthesis of other inorganic materials.

2. Experimental

All the chemicals in the experiments were analytical grade and used without further purification. The polymer, poly-(styrene-alt-maleic acid) (PSMA) (sodium salt, 13 wt.% aqueous solution), was purchased from Aldrich. The barium chloride dihydrate ($BaCl_2{\cdot}2H_2O$) was used as barium source and sodium molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$) as molybdenum source. In all cases, the concentrations of both $BaCl_2$ and Na_2MoO_4 were 0.1 m/L. The typical procedure is described as follows: designed volume (i.e. 0.25 mL, 1.0 mL and 2.0 mL, respectively) of PSMA aqueous solution was diluted by 1 L distilled water, 5.0 mL $BaCl_2$ aqueous solution then were added into 80 mL of the diluted PSMA aqueous solution with vigorous stirring. Subsequently, exactly same volume aqueous solution of Na_2MoO_4 was quickly injected into the above solution. Next, the mixed solution was stirred for 1 min by using a magnetic whisk. During the precipitation process, the reaction systems were kept at room temperature for 24 h. The final white precipitates were washed several times with distilled water, then dried at 30 °C in a desiccator for at least 10 h and stored for further characterization.

The crystal structures of the as-prepared precipitates were analyzed by X-ray diffraction (XRD) using the X-ray diffractometer (PANalyticalX'Pert PRO MPD) with Cu Kα radiation ($\lambda = 0.154$ nm) in a 2θ range of 20–70°. The morphologies of the as-prepared $BaMoO_4$ were characterized by field emission scanning electron microscope (FE-SEM, Hitachi S-4800). Room temperature PL spectra were recorded on a LabRAM Aramis Raman spectrometer with a He–Cd laser ($\lambda = 325$ nm) as an excitation source.

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3. Results and discussion

Fig. 1 shows the typical XRD patterns of the as-prepared precipitates obtained at different PSMA concentration. All the diffraction peaks can be readily indexed to the pure scheelite-type tetragonal structure of $BaMoO_4$ (space group: $I4_1/a$), which are in good agreement with the literature values (JCPDS Card, No. 29-0193). No additional phase peaks were observed in the resolution range, indicating that the pure tetragonal phase $BaMoO_4$ can be obtained at different concentrations of both reactants and PSMA. The strong and sharp diffraction peaks suggested the synthesized crystals were well-crystallized. Moreover, the intensities of the strong peak (1 1 2) are almost same in the three samples, indicating that the PSMA concentration has no effects on the phase structure and crystallinity.

Fig. 2 summarizes the morphological evolution of $BaMoO_4$ as a function of concentrations of both reactants and PSMA. When PSMA = 2 mL/L, i.e. the high concentration of PSMA, the morphology of $BaMoO_4$ changed dramatically as the concentrations of reactants was increased (sample A1 to A7). At low concentration of reactants, only a few irregular crystals formed (A1), and then their morphologies experienced a three-stage transition, the pure flower-like spheres, a mixed morphology of flower-like spheres and spindle-like crystals, and the pure spindle-like crystals, respectively. Similar to the phenomena at high concentration of PSMA, the morphologies of $BaMoO_4$ also underwent such an analogous transition at a moderate PSMA concentration (PSMA = 1 mL/L, sample B1 to B7). However, the differences were: (i) the quantity of petals of flower-like spheres in group B increased and their sizes diminished, (ii) the spindle-like crystals in group A were changed into big octahedrons with sharp edges in group B, (iii) the last transition stage, the pure octahedral crystals disappeared in group B. In contrast to the above groups, the morphology evolution at low PSMA concentration (PSMA = 0.25 mL/L, sample C1 to C7) was a gradual and continuous process from ellipsoids to elongated octahedrons. Furthermore, the flower-like spheres disappeared. It is important to note that, under the conditions of extremely low amounts of reactants (sample A1, B1 and C1, 0.1 mM $BaCl_2$ and 0.1 mM Na_2MoO_4), only in sample C1 the regular ellipsoidal crystals with long axis of 1–1.5 μm were observed. Ignoring the absolute sizes caused by fluctuation effect and the interaction of the crystallization, the long axis length and short axis length ratios in group C have a positive correlation with the concentrations of reactants.

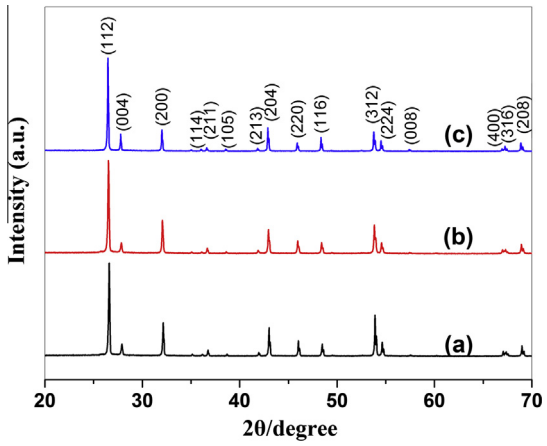

Fig. 1. XRD patterns of the final precipitates obtained at the following typical experimental concentrations: (A) 1.0 mL/L PSMA, 0.5 mM $BaCl_2$ and 0.5 mM Na_2MoO_4 (B) 2.0 mL/L PSMA, 0.7 mM $BaCl_2$ and 0.7 mM Na_2MoO_4, (C) 0.25 mL/L PSMA, 0.3 mM $BaCl_2$ and 0.3 mM Na_2MoO_4.

In our previous work, the morphology evolution of $BaMoO_4$ crystals from spheres to octahedrons under the control of poly (sodium4-styrene-sulfonate) (PSS) were investigated [47]. We proposed that the PSS controls the morphology and size of crystals by inhibiting the oriented growth direction. Since the above experimental result is so consistent with the group C, we suggest that the controlling mechanism of PSS also can be applied for this purpose. A schematic formation mechanism of $BaMoO_4$ crystals at low PSMA concentration is shown in Fig. 3a. As an effective crystal growth modifier with carboxyl group, PSMA is negatively charged when it is in the aqueous solution. Based on this reason, PSMA has a tendency to attract cations or attach on the positively charged crystal surface. At first, PSMA attracts Ba^{2+}, forming the PSMA–Ba chain, then the PSMA–Ba chain will attach to the exposed planes of $BaMoO_4$ crystals. However, different exposed planes of crystals

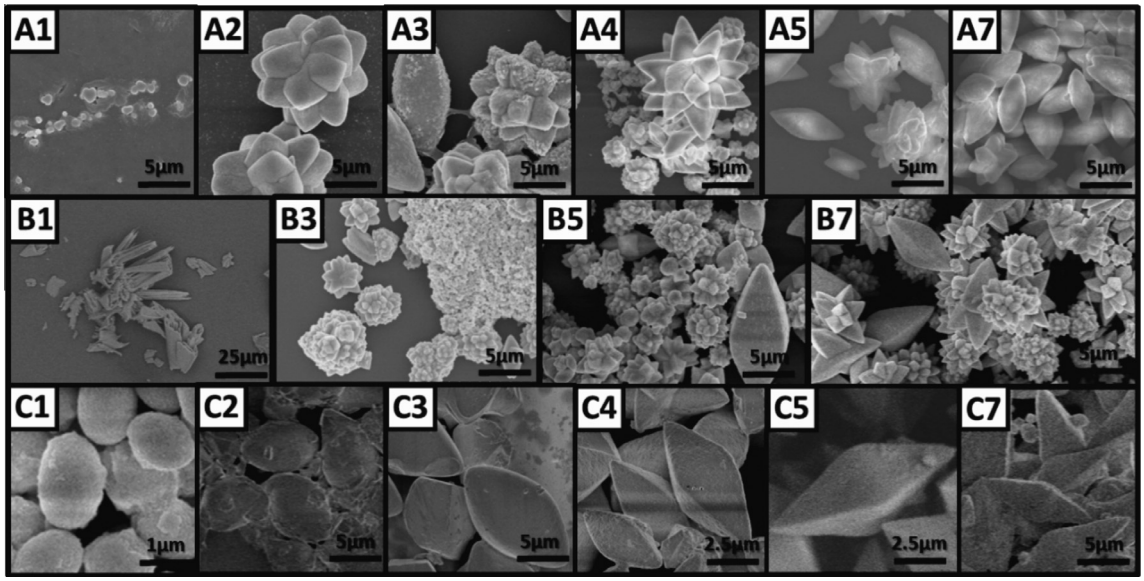

Fig. 2. Morphology of $BaMoO_4$ obtained at different concentrations of both reactants and PSMA. *The letter represents the concentration of PSMA, i.e. A = 2 mL/L, B = 1 mL/L and C = 0.25 mL/L, respectively. The number represents the dosages of the reactants (unit: 0.1 mM). For example, the title "A5" means 2 mL/L PSMA, 0.5 mM $BaCl_2$ and 0.5 mM Na_2MoO_4.