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Controllable route to barium molybdate crystal and their photoluminescence



ALLOYS AND COMPOUNDS

M. Lei^a, C.X. Ye^a, S.S. Ding^a, K. Bi^a, H. Xiao^a, Z.B. Sun^{b,*}, D.Y. Fan^a, H.J. Yang^a, Y.G. Wang^{a,*}

^a State Key Laboratory of Information Photonics and Optical Communications & School of Science, Beijing University of Posts and Telecommunications, Beijing 100876, China ^b Center for Space Science and Applied Research, National Space Science Center, Chinese Academy of Sciences, Beijing 100190, China

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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 CaCO₃ [31–33], BaSO₄ [34,35], BaCO₃ [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, BaMoO₄ 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 BaMoO₄, 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 BaMoO₄ has been rarely reported to date [47]. In this work, BaMoO₄ crystals with distinct morphologies were fabricated via a biomineralization route, by using the poly-(styrene-alt-maleic acid) (PSMA) as crystal growth modifier

ABSTRACT

A simple precipitation route has been developed to synthesize BaMoO₄ 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 BaMoO₄. 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 ${}^{1}T_{2} \rightarrow {}^{1}A_{1}$ transition in the intrinsic MoO₄²⁻ group. © 2015 Elsevier B.V. All rights reserved.

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 (BaCl₂·2H₂O) was used as barium source and sodium molybdate dihydrate (BaCl₂·2H₂O) was used as barium source and sodium molybdate dihydrate (Na₂MoO₄·2H₂O) as molybdenum source. In all cases, the concentrations of both BaCl₂ and Na₂MoO₄ 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 BaCl₂ aqueous solution then were added into 80 mL of the diluted PSMA aqueous solution with vigorous stirring. Subsequently, exactly same volume aqueous 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 K α radiation (λ = 0.154 nm) in a 2 θ range of 20–70°. The morphologies of the as-prepared BaMoO₄ 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 (λ = 325 nm) as an excitation source.



^{*} Corresponding authors. Tel./fax: +86 10 62282050.

E-mail addresses: zbsunnssc@sohu.com (Z.B. Sun), wangyg@bupt.edu.cn (Y.G. Wang).

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 (112) 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



Fig. 1. XRD patterns of the final precipitates obtained at the following typical experimental concentrations: (A) 1.0 mL/L PSMA, 0.5 mM BaCl₂ and 0.5 mM Na₂MoO₄ (B) 2.0 mL/L PSMA, 0.7 mM BaCl₂ and 0.7 mM Na₂MoO₄, (C) 0.25 mL/L PSMA, 0.3 mM BaCl₂ and 0.3 mM Na₂MoO₄.

of BaMoO₄ 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 BaMoO₄ 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 BaCl₂ and 0.1 mM Na₂MoO₄), only in sample C1 the regular ellipsoidal crystals with long axis of $1-1.5 \,\mu m$ 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.

In our previous work, the morphology evolution of BaMoO₄ 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 BaMoO₄ 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 Ba²⁺, forming the PSMA–Ba chain, then the PSMA–Ba chain will attach to the exposed planes of BaMoO₄ crystals. However, different exposed planes of crystals



Fig. 2. Morphology of BaMoO₄ 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 BaCl₂ and 0.5 mM Na₂MoO₄.



Fig. 3. Schematic formation mechanisms of BaMoO₄ crystals at different concentrations of both PSMA and reactants.

usually have different surface energies, and it is known that crystal plane with high surface energy grows faster than those with lower surface energy. PSMA will selectively adsorb on the high-surfaceenergy plane, decreasing the local Ba²⁺ concentration by forming new PSMA-Ba chain, and inhibiting crystal growth in this direction by lowering the surface energy. When PSMA is sufficient, the inhibition in the initially dominant growth directions will be obvious, causing the morphology of ellipsoid. On the contrary, an increase in reactants concentration will weaken such inhibition. explaining the morphology evolution from ellipsoid to elongated octahedron in group C. These results agree with the analysis of Yu et al. in that the morphology of crystal is determined by the adsorptive feature of different PSMA concentration [48]. In addition, when the local PSMA concentration is much higher than the Ba²⁺ concentration, the strong PSMA-Ba complexion will intensively decline the combination of Ba^{2+} and MoO_4^{2-} , leading to the incomplete or irregular crystal morphology (sample A1 and B1).

Fig. 3b shows the schematic evolution mechanisms of the octahedron or spindle-like to flower-like crystal at moderate or high PSMA concentration. This transformation process could also be ascribed to the inhibition of PSMA. Unlike low PSMA concentration, as PSMA/Ba²⁺ ratio increases, the surface energy of those original preferential-growth crystal planes will lower to an extent that almost identical to that of other crystal planes, thus the crystal will not only grow along the long axis, but also have the potential to grow along other direction, achieving the transformation from one-dimensional growth to multi-dimensional growth. When the PSMA/Ba²⁺ ratio is low, the samples will exhibit distinct crystalline characteristics at different absolute PSMA concentration. At moderate PSMA concentration (Fig. 3b, left), two kinds of crystal morphologies could coexist. It appears that part of the octahedral nuclei will form the flower-like crystals whereas the remaining nuclei will grow into big octahedrons. Conversely, local high PSMA will modulate the growth of nuclei directly, forming the spindle-like nuclei (Fig. 3b, right). This may explain the sharpness of the crystal edge and the morphology evolution at two different PSMA concentrations. It is also found that the number of particles



Fig. 4. Room temperature PL spectra of BaMoO₄ obtained at the following typical experimental concentrations (a) 1.0 mL/L PSMA, 0.5 mM BaCl₂ and 0.5 mM Na₂MoO₄ (b) 2.0 mL/L PSMA, 0.7 mM BaCl₂ and 0.7 mM Na₂MoO₄, (c) 0.25 mL/L PSMA, 0.3 mM BaCl₂ and 0.3 mM Na₂MoO₄.

reduced while their volumes increased as the PSMA/Ba²⁺ ratio increases. This may occur because of the well-known Ostwald Ripening process [49] that the small crystals dissolve first and then redeposit onto larger crystals to maintain the minimum system energy. When the local PSMA concentration is high but not enough to completely inhibit the crystallization of BaMoO₄, large particles usually have lower energy and thus more stable than the small particles, promoting the Ostwald Ripening process.

The optical properties of BaMoO₄ nanocrystals were investigated by the photoluminescence (PL) technique. Fig. 4 illustrates the PL spectra of the typical BaMoO₄ samples with excitation wavelength of 325 nm at room temperature. The samples exhibit broad green emission peaks of 530 nm, which is consistent with previous data [26,50,51]. It is well accepted that the emission spectra of metal molybdates are mainly caused by the electronic charge transfer within the MoO_4^{2-} unit [27,52]. Previous reports [53,54] analyze the PL spectra of compounds by the Peakfit deconvolution program. Based on this method, the PL spectra of BaMoO₄ can be deconvolved into several Gaussian peaks. Using Sample A as an example, we can get five component curves at 410 nm (8%), 445 nm (13%), 493 nm (16%), 525 nm (48%) and 595 nm (15%), which represents different types of electronic transitions and specific atomic arrangements. Abreu et al. [54] attribute the blue-green emission to an ordered structure with shallow defects, while the yellow-orange-red emission is caused by a disordered structure with deep defects. According to the principle of MoO₄²⁻ complexes, the coupling between the O-2p (σ) and O-2p (π) orbitals and Mo-4d (t₂) and Mo4d (e) orbitals are responsible for the hybridization of molecular orbitals. Among those electron states, only the ${}^{1}T_{2} \rightarrow {}^{1}A_{1}$ transition is allowed [27,55]. We ascribe the blue and green emission to ${}^{1}T_{2} \rightarrow {}^{1}A_{1}$ transition in the intrinsic MoO_4^{2-} group (shallow defects) and the orange emission to the defect MoO₃ group (deep defects) [56]. The additional emissions can be explained by the Jahn–Teller splitting effect [31]. In particular, our previous study on the photoluminescence of BaMoO₄ shows intense blue emission and weak green emission at the same wavelengths [56], we conjecture this may induced by differences in the crystal structures. However, accurate explanation for the PL spectra of BaMoO₄ remains to be further explored. There are many factors that govern the photoluminescence properties of BaMoO₄, such as particle size, crystalline degree, morphology, and surface defects [55,56]. As is shown in Fig. 4, homogeneous distribution and small particle size are important factors to enhance the PL intensity, for crystals with such morphology usually have fewer dead layers [31,47].

4. Conclusions

In this study, BaMoO₄ crystals with diverse morphologies have been synthesized by using PSMA as crystal growth modifier via a biomineralization route. The formation mechanisms of the as-prepared BaMoO₄ crystals at different concentrations of both reactants and PSMA were discussed in detail. PSMA controls the crystal morphology mainly by inhibiting the oriented growth direction, and higher PSMA concentration will cause the transformation from one-dimensional growth to multi-dimensional growth. Room temperature photoluminescence (PL) spectra show the maximum emission peaks at 530 nm, which is ascribed to the ${}^{1}T_{2} \rightarrow {}^{1}A_{1}$ transition in the intrinsic MoO₄²⁻ group. Homogeneous distribution and small particle size are important factors to enhance the PL intensity.

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