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# Microwave-assisted synthesis of BaMoO<sub>4</sub> nanocrystallites by a citrate complex method and their anisotropic aggregation

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#### Abstract

BaMoO<sub>4</sub> powders, which have scheelite-type structure, were successfully synthesized at low temperatures by a modified citrate complex method assisted by microwave irradiation. The citrate complex precursors were heat-treated at temperatures from 300 to 500 °C for 3 h. Crystallization of the BaMoO<sub>4</sub> powders were detected at 350 °C and completed at a temperature of 400 °C. TEM image of the BaMoO<sub>4</sub> product heat-treated at 400 °C revealed spindle-rods-like and flake-like morphology at 500 °C. The anisotropic aggregation habit of BaMoO<sub>4</sub> lead to two-dimensionally aggregated powder morphology, which was attributed to the high chemical potentials of the intrinsic structure of BaMoO<sub>4</sub>.

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Keywords: BaMoO<sub>4</sub>; Citrate complex method; Anisotropic aggregation; Assembling process

#### 1. Introduction

BaMoO<sub>4</sub> is an important inorganic material that has a high application potential in various fields, such as in photoluminescence [1] and hosts for lanthanide-activated lasers [2]. BaMoO<sub>4</sub> has usually been prepared by conventional methods consisting of repeated ball-milling and solid-state reaction of BaCO<sub>3</sub> and MoO<sub>3</sub> powders [3]. However, BaMoO<sub>4</sub> powders prepared by the solid-state reaction are relatively large with inhomogeneous morphology and composition. Inhomogeneous compounds of BaMoO<sub>4</sub> might be easily formed because MoO<sub>3</sub> has a tendency to vaporize at high temperatures [4].

These problems could be solved via an advanced wet chemical route. Polymerized complex method as a modified Pechini method [5], where several metal ions in a solution could be first chelated to form metal complexes and then polymerized to form a gel, seems to be most suitable among chemical solution processes, because rigidly fixed cations are homogeneously dispersed in the polymer network and have few chances to segregate even during pyrolysis. However, in spite of many advantages of the polymerized complex method, the weakness of this method is the difficulty of the effective removal of the large amount of organic substances [6]. Based on this consideration, the citrate complex method with different solvents as chemical solution process was tried in this work for the synthesis of BaMoO<sub>4</sub> nanopowders. In this process, metal citrate complexes without a network structure are formed by using water instead of ethylene glycol.

On the other hand, microwave irradiation as a heating source has been found and developed for a number of applications in chemical and ceramic processing [7–9]. Compared with the usual methods, microwave synthesis has the advantages of shortening reaction time, giving products with small particle size, narrow particle size distribution and high purity. Jansen et al. [7] suggested that these advantages could be attributed to fast homogeneous nucleation and easy dissolution of the gel.

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In this work, we report the synthesis of BaMoO<sub>4</sub> nanopowders from citrate complex precursor assisted by microwave irradiation and focus on the aggregation behavior of BaMoO<sub>4</sub> nanopowders as a function of heating temperature. The precursors and powders were evaluated through their crystallization process, thermal decomposition and by identifying the particle morphology.

### 2. Experimental

Barium carbonate (BaCO<sub>3</sub>, Junsei Chemical Co. Ltd., Japan) and ammonium molybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub> O<sub>24</sub>·4H<sub>2</sub>O, Fluka Chemical Co. Ltd., Japan) were used as the metallic cations. De-ionized water (DW) and citric acid (HOC(CO<sub>2</sub>H)(CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, CA, Yukiri Pure Chemical Co. Ltd., Japan) were used as the solvent and chelating agent for the process. Fig. 1 shows the schematic flow chart for the synthesis of BaMoO<sub>4</sub> powders by the modified citrate complex method assisted by microwave irradiation. The citrate solution was prepared by dissolving appropriate molar ratios of citric acid in de-ionized water (CA:DW molar ratio = 1:4). After complete homogenization of the citrate solution, barium carbonate and ammonium molybdate tetrahydrate were dissolved in the molar ratio of total chelate metal cations (TO) and citric acid (TO:CA molar ratio = 1:5). By keeping the solution at a temperature of 100 °C for 1 h under constant stirring, the solution became viscous. A microwave irradiation system with 1200W (2.45 GHz) was used for the reactions in the solution. The solution was placed in the microwave oven and the reaction was performed under ambient air for 30 min. The working cycle of the microwave



Fig. 1. Flow chart for synthesis of BaMoO<sub>4</sub> powders by the modified citrate complex method using microwave irradiation.

oven was set between 40 s on and 20 s off. The solution became more viscous with time and its color changed to brown. No visible precipitation was observed during the heating process. As this solution condensed, the brown product was converted into powders after grinding with a Teflon bar. Thermal analysis was performed on this powder, hereinafter referred to as the 'precursor'. Heat-treatment of the precursor was performed at various temperatures from 300 to 500 °C for 3 h.

The crystallization process of the polymeric precursor was evaluated by thermogravimetry–differential thermal analysis (TG–DTA, SETRAM, France), using a sample weight of about 10 mg and a heating rate of 5 °C/min. The existing phase in the particles after heat-treatment was identified by ordinary X-ray diffraction (XRD, Cu K $\alpha$ , 40 kV, 30 mA, Rigaku, Japan) with a scan rate of 3 °/min. The microstructure and surface morphology of the powders were observed by transmission electron microscopy (TEM, JEM 2010, JEOL).

### 3. Results and discussion

# 3.1. Synthesis of BaMoO<sub>4</sub> nanopowders and crystallization process

The crystallization process of the precursor was evaluated by XRD, TG–DTA and electronic diffraction pattern (EDP). Fig. 2 shows the phase identification of the BaMoO<sub>4</sub> powders heat-treated for 3 h as a function of heating temperature in detail using XRD. In Fig. 2(a), the powders of BaMoO<sub>4</sub> at 300 °C were amorphous without any crystallized phases. Above 350 °C in Fig. 2(b–e), the powders could be identified as BaMoO<sub>4</sub> phases, and unreacted or additional phases were not detected.

Fig. 3 shows the TG–DTA curves for the BaMoO<sub>4</sub> precursor. In Fig. 3, with the increase of temperature, the weight loss occurs in the TG curve up to  $470 \,^{\circ}$ C. Thereafter the weight



Fig. 2. XRD patterns of the BaMoO<sub>4</sub> powders heat-treated at (a) 300, (b) 350, (c) 400, (d) 450 and (e) 500  $^\circ C$  for 3 h.



Fig. 3. TG-DTA curves of the BaMoO<sub>4</sub> precursor in flowing air.

remains constant, indicating that the decomposition of all organic materials continued in the precursor, their combustion and crystallization of BaMoO<sub>4</sub> have been below 470  $^{\circ}$ C. No significant plateau, corresponding to well-defined intermediate products, appeared in the heating process. The DTA

curve in Fig. 3 could be interpreted by two physical meanings: (1) increase of DT curve from  $350 \,^{\circ}$ C corresponds to initial decomposition of the precursor and nucleation of the nanocrystalline BaMoO<sub>4</sub> and (2) exothermic peak at 445  $^{\circ}$ C corresponds to the crystallization of BaMoO<sub>4</sub>. Below  $350 \,^{\circ}$ C, the resultant particles were dark brown and porous in structure, denoting an amorphous phase. It is attributed to contain a lot of carbons and ignitable organics. When the temperature further increases above  $350 \,^{\circ}$ C, crystal nuclei begin to form and consequently the primary crystallization process is completed accompanying the combustion of the residual carbons and ignitable organics.

Fig. 4 shows electronic diffraction pattern and morphology change of the BaMoO<sub>4</sub> powders prepared from 300 to  $500 \degree$ C. The EDP of BaMoO<sub>4</sub> powders heat-treated at  $300 \degree$ C in Fig. 4(a) shows only diffuse hollow rings, corresponding to an amorphous phase. At  $350 \degree$ C in Fig. 4(b), dotted rings were observed, signifying the nanocrystalline formation. In Fig. 4(c), the products obtained at  $400 \degree$ C reveal spindle-rodslike aggregated morphology, which are composed of tiny nanoparticles. In Fig. 4(d), the BaMoO<sub>4</sub> products obtained at  $500 \degree$ C clearly reveal flake-like morphology with an aver-



Fig. 4. TEM and EDP of BaMoO<sub>4</sub> powders heat-treated at (a) 300, (b) 350, (c) 400 and (d) 500 °C for 3 h.

age diameter of between 50 and 100 nm and lengths up to 500 nm.

# 3.2. Formation mechanism of anisotropic aggregation in $BaMoO_4$ system

In general, when synthesizing nanoparticles from precursor, nucleation is very fast and subsequent growth occurs by two primary mechanisms: coarsening (also known as Ostwald ripening [10]) and aggregation process [11–15]. Coarsening processes contrive the growth of larger crystals at the expense of smaller crystals as described by the Gibbs–Thomson equation [16]. Crystal growth from aggregation can occur, producing particle assemblies accumulated from randomly oriented to highly oriented nanoparticles [11–13]. Anisotropic aggregation is an important mode for crystal growth. Primary particles may aggregate in an oriented accumulation to produce larger particles, or they may aggregate randomly [14,15].

The present system is a typical oriented aggregation process involving coarsening process. Fig. 5 shows that schematic diagram of a possible arranging process of BaMoO<sub>4</sub> nanopowders for the two-dimensionally assembled morphology as a function of heating temperature. Amorphous nanoparticles in Fig. 4(a) acted as the precursor for the synthesis of BaMoO<sub>4</sub> nanopowders. Nanocrystalline nuclei were formed in the precursor following the coarsening at 350 °C in Fig. 4(b). And the larger particles grew at the cost of the small ones, due to the difference of surface energy between the large particles and the smaller particles, according to the well-known Gibbs–Thomson law [16].



Fig. 5. Schematic diagram of two-dimensional representation of aggregation growth mechanism.

At 400 °C, in Fig. 4(c) the spindle-rods-like aggregates coexisted with different lengths and irregular morphology of nanoparticles. This anisotropic aggregation habit can be considered under the viewpoint of the intrinsic structure of the BaMoO<sub>4</sub>. Fig. 6 shows the BaMoO<sub>4</sub> structure viewed along the *a*-axis for the structural feature of the (100) faces. In particular, the special feature of the (100) face and all the negative  $[MoO_4^{2-}]$  chain lies on the (100) face. All the negative  $[MoO_4^{2-}]$  anions are exposed, while all the positive Ba<sup>2+</sup> ions are shielded [17]. The (100) faces of BaMoO<sub>4</sub> contain units fully composed of highly distorted tetrahedral-Mo with dangling bonds, whereas the deformed octahedral Ba-chain was shielded by the chains of tetrahedral-Mo. These chains exist along the *a*-axis alternatively, which makes the (100)face perpendicular to the *a*-axis with the highest chemical potential among other facets, such as (001) and (010) [18]. This structural feature makes the (100) faces very active to the surrounding growth conditions. It is this structural feature that plays a key role in the highly intrinsic preferential growth along the axis of the BaMoO<sub>4</sub> aggregates.

As the reaction proceeded at a higher temperature in Fig. 4(d), the irregular nanoparticles disappeared and flakelike aggregates were formed. It is considered that the flakelike aggregates were formed by a horizontally assembling process of the spindle-rods-like aggregates as shown in Fig. 5(d) and (e). Fig. 7(a) shows a typical TEM image of aggregated BaMoO<sub>4</sub> particles prepared at 400 °C. The upper image shows a spindle-rods-like crystal constructed from at least several primary BaMoO<sub>4</sub> nanocrystallites. Schematic white-dotted outlines in below image show one possible attachment scheme that could give rise to the observed onedimensionally anisotropic aggregation morphology. Fig. 7(b) shows an elongated and assembled crystal prepared at 500 °C. It is constructed of three primary aggregated building blocks. The white-dotted lines in the bottom image highlight the four regions of the assembled flake-like aggregate.



Fig. 6. BaMoO<sub>4</sub> structure viewed along the *a*-axis for the structural feature of the  $(1\,0\,0)$  faces.



Fig. 7. TEM image of aggregated BaMoO<sub>4</sub> particles heat-treated at (a) 400 and (b)  $500 \degree C$  for 3 h.

#### 4. Summary

BaMoO<sub>4</sub> powders were successfully synthesized at low temperature by the modified citrate complex method using microwave irradiation. Crystallization of BaMoO<sub>4</sub> powders were detected at 350 °C and completed at 400 °C. The products obtained at 400 °C revealed spindle-rods-like aggregation. The anisotropic aggregation was attributed to the extremely high anisotropic chemical potentials of the intrinsic scheelite structure. As the reaction proceeded at a higher temperature, 500 °C, flake-like aggregates were observed, which were formed by a horizontal assembly of the spindlerods-like aggregates.

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