Synthesis of Al₂(MoO₄)₃ by Two Distinct Processes, Hydrothermal Reaction and Solid-State Reaction

Yuhei Matsumoto, Rie Shimanouchi*

Faculty of Science, Kochi University, 2-5-1, Akebono-cho, Kochi city, Kochi 780-8520, Japan

Abstract

Al₂(MoO₄)₃ could be synthesized using two different methods, the traditional solid-state reaction and the hydrothermal reaction with post-heating. For preparation by the solid-state reaction, the starting materials were Al(OH)₃ and MoO₃. TG-DTA results suggested that the reaction temperature of the solid-state reaction should be more than 973 K for crystallization of Al₂(MoO₄)₃. In contrast, the hydrothermal technique required crystallization at lower temperatures. SEM photographs indicate that while the former yields larger particles, the latter yields finer and well-shaped particles. It is hoped that Al₂(MoO₄)₃ obtained by this method will find applications in the manufacture of ceramic devices.

Keywords: Hydrothermal synthesis; Alminum molybdate; Powder synthesis; Ceramics materials

1. Introduction

Solid electrolytes are expected to find wide-ranging practical applications in functional devices such as gas sensors [1-3] and solid oxide fuel cells [4-6]. Some solid electrolytes have already been used commercially as sensors in biomedical and industrial devices [7, 8]. However, trivalent cations are regarded as a poor migrant species in solids because of the strong electrostatic interactions between the cation and the lattice-forming anions that surround the cation.

* Corresponding author.

E-mail address: rshima@kochi-u.ac.jp
Sc$_2$(WO$_4$)$_3$-type crystal structures are well known as trivalent cation conductors in solid electrolytes. Many studies have focused on the preparation and electric properties of similar tungstates [9-12]. In this study, we focused on Al$_2$(MoO$_4$)$_3$, which possesses an Sc$_2$(WO$_4$)$_3$-type crystal structure. Previous studies have investigated Al$_2$(WO$_4$)$_3$ structures with regard to their electrical properties and aluminum ionic conduction[13, 14]. These aluminum ionic conductors can be expected the application to batteries and sensors as well as other ionic conductors [15]. The aluminum ion has the smallest ionic radius, making it suitable for ionic conduction in solids. Additionally, aluminum-containing materials are typically inexpensive.

In Sc$_2$(WO$_4$)$_3$-type crystal structure, oxide anions in the tungstates are strongly bonded to tungsten ions; thus, the interaction between the trivalent cations and the oxide anions is reduced. The ionic radius of hexavalent molybdenum (Mo$^{6+}$), 0.055 nm, is smaller than that of hexavalent tungsten (W$^{6+}$), 0.056 nm. Therefore, the mobility of the trivalent cations in molybdates with Sc$_2$(WO$_4$)$_3$-type structure is enhanced relative to that in tungstates. The ionic radii of both ions were referred by Shannon’s ionic radius with coordination number 6[16].

Furthermore, the electrical properties of solid materials depend on the synthesis method and conditions. Hydrothermal synthesis is known to be suitable for producing fine and well-crystallized ceramic powders [17]. It requires lower temperatures and shorter reaction times than solid-state reactions. Herein, we detail the synthesis and characterization of Al$_2$(MoO$_4$)$_3$ by both the solid-state and the hydrothermal reaction.

2. Experimental

For preparation by the solid-state reaction, the starting materials used are aluminum hydroxide (Al(OH)$_3$, 95%) and molybdenum (VI) oxide (MoO$_3$, 99.0%). These are mixed in a stoichiometric ratio, following which they are ball-milled and then calcined at 573 K for 6 h in air. The mixture was pulverized with a pestle and mortar and then calcined at 973 K for 12 h in air.

For preparation by the hydrothermal reaction, the starting materials used are aluminum nitrate hydrate (Al(NO$_3$)$_3$·9H$_2$O, 98.0%) and molybdenum powder (Mo, 99.9%). An aqueous solution of these materials was poured into a Teflon-lined mini-autoclave, which was then filled to 40% of its capacity with deionized water. The vessel was heated in an electric furnace for 5 h at 523 K. After the vessel was cooled in air, the product was recovered by filtration; washed with distilled, deionized water; and dried in a desiccator at room temperature. The obtained sample was heated at various temperatures in an electric furnace.

X-ray powder diffraction (XRD) measurements were carried out in the 2θ range from 5° to 75° using a Rigaku RINT-2000 X-ray diffractometer operating at 40 kV and 20 mA using Cu-Kα radiation. Thermogravimetric and differential thermal analysis (TG-DTA, MAC Science TG-DTA2000) were carried out at a heating rate of 10 K/min. from room temperature to 1273 K. The microstructures of the products were observed using a scanning electron microscope (SEM, JSM-6500F).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the sample obtained by the solid-state reaction. The diffraction pattern of the sample calcined at 573 K for 6 h is similar to the MoO$_3$ pattern. That of the sample calcined at 973 K for 12 h is identical to the Al$_2$(MoO$_4$)$_3$ pattern. Single-phase Al$_2$(MoO$_4$)$_3$ could be obtained by calcination at 573 K for 6 h and at 973 K for 12 h. Fig. 2 shows the TG-DTA curves of the mixture of Al(OH)$_3$ and MoO$_3$ as starting materials after ball-milling for 5 h. Approximately 7% weight loss can be observed at 255 – 300°C in the TG curve, and the corresponding endothermic peak appears at approximately 560 K in the DTA curve. We attribute this weight loss to the dissolution of Al(OH)$_3$. 
Fig. 1 indicated trace amounts of MoO$_3$ but none of Al$_2$O$_3$ at a reaction temperature of 573 K. This indicates that Al(OH)$_3$ transforms into amorphous Al$_2$O$_3$ by calcination at high temperature. Furthermore, approximately 2.3 % weight loss can be observed at 923 – 1063 K in the TG curve, and the corresponding endothermic peak appears at approximately 968 K in the DTA curve, as shown in Fig. 2. Thus, the endothermic peak can be attributed to the crystallization of Al$_2$(MoO$_4$)$_3$. These results suggest that the reaction temperature of the solid-state reaction should be more than 973 K for crystallization.

Fig. 3 shows the X-ray diffraction patterns of the sample obtained by the hydrothermal reaction and the heated samples at a 753 – 1273 K after hydrothermal synthesis. The desired material Al$_2$(MoO$_4$)$_3$ was not obtained by the hydrothermal reaction. Fig. 4 shows the TG-DTA curves after the hydrothermal reaction process with a molar ratio of starting materials, Al : Mo = 4 : 6. The weight loss and the corresponding endothermic peaks are observed at approximately 693 K, 813 K and 1243 K, as shown in Fig. 4. The XRD patterns shown in Fig. 3 exhibit similar phase changes at each heating temperature. The diffraction peaks of Al$_2$(MoO$_4$)$_3$ were observed in the XRD patterns of the sample heated at 843 K for 1 h, but not in those of the sample heated at 753 K for 1 h, as shown in Fig. 3. This result indicates that Al$_2$(MoO$_4$)$_3$ is crystallized at 843 K with a DTA endothermic peak. Single-phase Al$_2$(MoO$_4$)$_3$

Fig. 1. XRD patterns of sample synthesized by solid-state reaction between Al(OH)$_3$ and MoO$_3$ at 573 K for 6 h (a) and samples sintered at 973 K for 12 h (b).

Fig. 2. TG-DTA curves of sample of mixture of Al(OH)$_3$ and MoO$_3$ as starting materials after ball-milling for 5 h.

Fig. 3. X-ray powder diffraction patterns of sample synthesized by hydrothermal reaction at 250°C for 5 h (a), post-heated at 753 K for 1 h (b), at 843 K for 1 h (c), and at 1023 K for 3 h (d), and the sample after TG-DTA measurement from room temperature to 1273 K (e).

Fig. 4. TG-DTA curves of samples obtained by hydrothermal reaction process.
with an orthorhombic symmetry (space group Pbcn) could be obtained by post-heating the product synthesized hydrothermally at more than 843 K.

Al₂(MoO₄)₃ particles having Sc₂(WO₄)₃-type crystal structure synthesized by both methods were characterized by SEM. SEM photographs of the samples synthesized by the solid-state reaction are shown in Fig. 5. Fig. 5 (a) shows particles of the mixture of Al(OH)₃ and MoO₃ as starting materials after calcination at 573 K for 6 h. The majority of the powder consists of approximately 2-μm-size stick particles. In contrast, in the sample calcined at 973 K for 12 h, particle lengths of 3 – 5 and approximately 10 μm were observed, as shown in Fig. 5 (b). Particle size increased with the synthesis temperature.

SEM photographs of the powders prepared by the hydrothermal reaction and post-heating are shown in Fig. 6. They show photographs of the samples heated at reaction temperatures of 523 K for 5 h, 843 K for 1 h, and 1023 K for 3 h, respectively. In Fig. 6 (a), the majority of the powder consists of approximately 1-μm-size particles. In Fig. 6 (b), some particle growth is evident. In Fig. 6 (c), the most well-shaped particles with sizes of 0.5 – 1 μm are observed. The particle size of the sample prepared at 1023 K for 3 h was smaller than that of the sample prepared at 843 K for 1 h. These results indicate that the solid-state reaction affords larger particles; however, the hydrothermal reaction affords finer powder through post-heating. Products synthesized by the hydrothermal reaction crystallize to Al₂(MoO₄)₃ at lower temperatures of around 843 K, relative to those of 973 K in the case of the solid-state reaction.

Fig. 5. SEM photographs of samples synthesized by solid-state reaction at 573 K for 6 h (a) and samples sintered at 973 K for 12 h (b).

Fig. 6. SEM photographs of samples synthesized by hydrothermal reaction at 250°C for 5 h (a), post-heated at 570°C for 1 h (b), and at 750°C for 3 h (c).
4. Conclusions

In summary, $\text{Al}_2(\text{MoO}_4)_3$ can be synthesized using two different methods, the traditional solid-state reaction and the hydrothermal reaction with post-heating. The former requires calcination at high temperatures to crystallize $\text{Al}_2(\text{MoO}_4)_3$ from the oxides used as starting materials. In contrast, the latter requires crystallization at lower temperatures. In addition, SEM photographs indicate that while the former yields larger particles, the latter yields finer and well-shaped particles. It is hoped that $\text{Al}_2(\text{MoO}_4)_3$ obtained by this method will find applications in the manufacture of ceramic devices. Further investigations will be required in order to understand the interactions and electrical properties of the microstructures.

Acknowledgement

We thank Research Laboratory of Hydrothermal Chemistry, Kochi University, for supporting the preparation at high temperatures and measurement of Vickers hardness. We also thank the Center for Advanced Marine Core Research, Kochi University, for SEM-EDS measurements.

References