Crystal Growth of Molybdenum Oxides by Chemical Transport

Yoshichika Bando*, Yasutoshi Kato**, and Toshio Takada**

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Single crystals of MoO₂, MoO₃, and MoₙOₙ₋₁ (ₙ=4, 8, 9) were grown by chemical transport using TeCl₄ as transport agent. The electrical resistivities of the grown crystals were measured from liquid nitrogen temperature to room temperature.

I INTRODUCTION

There are many intermediate oxides such as MoₙO₂ₙ₋₁ between MoO₂ and MoO₃. The phase diagram of the Mo-O system showed that there are two distinct oxides, MoO₁₁ and Mo₂O₂₄ between MoO₂ and MoO₃. Kihlborg recognized five compounds as the intermediate oxides (MoₙOₙ₋₁), that is, Mo₄O₁₁, Mo₆O₁₄, Mo₉O₂₃, Mo₉O₂₆, and Mo₁₃O₃₈, of which Mo₄O₁₁ and Mo₉O₂₆ are dimorphic. These intermediate oxides are the Magneli phases whose crystal structures can be described on the basis of the ReO₃ type.

Chemical transport in the closed system has been applied to the growth of single crystal of the Magneli phases (VₙO₂ₙ₋₁, TiₙO₂ₙ₋₁) using TeCl₄ as transport agent. In crystal growth of Magneli phase, oxygen pressure is the important parameter which must be delicately adjusted to control the particular phase grown, because each phase is stable only in the narrow range of oxygen pressure. Authors recently succeeded in growing single crystals of VₙO₂ₙ₋₁ and TiₙO₂ₙ₋₁ by the chemical transport which had no need of the procedure of pressure control. The phase of single crystals (VₙO₂ₙ₋₁) obtained by this method was all the same as that of source material. Therefore, it was considered that the single crystals of MoₙO₂ₙ₋₁ were possible to be grown by the same method. We have much interested in the relation between the phase of source material and that of single crystals obtained.

II EXPERIMENTALS

Synthesis of source materials. Source materials for the chemical transport were synthesized from highly pure molybdenum dioxides and trioxide. Mixtures of MoO₃ and MoO₂ (3:1 in mole ratio) were pressed and placed in evacuated silica tube. The sealed tubes were heated at 550°C for 14 days in preparation of monoclinic MoO₁₁ and at 650°C for 5 days in preparation of orthorhombic MoO₁₁.

* Bando Yoshichika: Laboratory of Inorganic Synthesis, Institute for Chemical Research, Kyoto University, Uji, Kyoto.
** Kato Yasutoshi, Takada Toshio: Laboratory of Solid State Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.
Crystal Growth of Molybdenum Oxides

The products were confirmed as a single phase by X-ray diffraction. Powders of Mo₈O₂₅ and Mo₉O₂₆ were prepared from MoO₃ and Mo₄O₁₁. The sealed tubes containing the mixture of MoO₃ and Mo₄O₁₁ (4:1 in mole ratio) were heated at 700°C for 3 days in preparation of Mo₈O₂₅. The mixtures of MoO₃ and Mo₄O₁₁ (5:1 in mole ratio) in the sealed tube were heated at 750°C for 2 days to product monoclinic Mo₉O₂₆ and at 700°C for 3 days to product triclinic Mo₉O₂₆. These products were confirmed as a single phase by X-ray diffraction.

Chemical transport. The sealed tube for the chemical transport was prepared by the follows. Powder of molybdenum oxide (2 grams) was loaded at the end of transparent silica tube of 13 mm in diameter and 170 mm in length. TeCl₄ powder was added as transport agent into the silica tube. This procedure performed in a dry box to prevent TeCl₄ from deliquescence. After the tube was evacuated to 10⁻⁶ Torr, it was sealed off. The tube was kept in the horizontal electric furnace, where the source zone with the source material was heated at higher temperature and the crystallization zone at lower temperature. After the transport, the tube was quenched in water. In order to measure the transport rate, the crystals obtained at the crystallization zone were weighed.

Characterization of crystal. The crystals were identified by the X-ray powder method. Laue X-ray pictures were taken to confirm them to be single crystals. The measurement of electrical resistivity was carried out by means of four point method using a d.c. potentiometer.

III RESULTS

Table I shows the representative transport conditions for the growth of large crystals.

<table>
<thead>
<tr>
<th>Source materials (2 grams)</th>
<th>Temperature gradient (deg/degC)</th>
<th>TeCl₄ (mg/cc)</th>
<th>Transport time (hr)</th>
<th>Transport rate (mg/hr)</th>
<th>Transported material</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₃</td>
<td>700/630</td>
<td>3.0</td>
<td>70</td>
<td>10.3</td>
<td>MoO₂</td>
<td>reddish purple polyhedral</td>
</tr>
<tr>
<td>Mo₄O₁₁ (ortho.)</td>
<td>690/640</td>
<td>3.0</td>
<td>70</td>
<td>26.4</td>
<td>Mo₄O₁₁ (ortho.)</td>
<td>royal purple thin plate</td>
</tr>
<tr>
<td>Mo₄O₁₁ (ortho.)</td>
<td>650/560</td>
<td>3.0</td>
<td>50</td>
<td>31.0</td>
<td>Mo₄O₁₁ (monocli.)</td>
<td>royal purple thin plate</td>
</tr>
<tr>
<td>Mo₄O₁₁ (monocli.)</td>
<td>580/500</td>
<td>3.0</td>
<td>50</td>
<td>26.6</td>
<td>Mo₄O₁₁ (monocli.)</td>
<td>royal purple thin plate</td>
</tr>
<tr>
<td>Mo₉O₂₅</td>
<td>750/730</td>
<td>0.5</td>
<td>71</td>
<td>8.8</td>
<td>Mo₉O₂₅</td>
<td>purplish black</td>
</tr>
<tr>
<td>Mo₉O₂₆ (monocli.)</td>
<td>770/760</td>
<td>0.5</td>
<td>69</td>
<td>6.1</td>
<td>Mo₉O₂₆ (monocli.)</td>
<td>black</td>
</tr>
<tr>
<td>Mo₉O₂₆ (monocli.)</td>
<td>770/745</td>
<td>0.5</td>
<td>70</td>
<td>16.7</td>
<td>Mo₉O₂₆ (tricli.)</td>
<td>black needle</td>
</tr>
<tr>
<td>Mo₉O₂₆ (tricli.)</td>
<td>750/730</td>
<td>0.5</td>
<td>70</td>
<td>13.8</td>
<td>Mo₉O₂₆ (tricli.)</td>
<td>black needle</td>
</tr>
<tr>
<td>MoO₃</td>
<td>650/600</td>
<td>3.0</td>
<td>74</td>
<td>11.9</td>
<td>MoO₃</td>
<td>light yellow needle</td>
</tr>
</tbody>
</table>

(331)
crystals, the transport rate and the phases of obtained crystals. The composition of single crystals obtained was the same as that of source material. However, the phase of single crystals of Mo$_{80}$O$_{23}$ and Mo$_9$O$_{26}$ depended on the temperature of the crystallization zone, independently of the phase of source material. It was reported by Kihlborg$^{2}$ that the formation temperature by solid state reaction is 620$-$680°C for orthorhombic Mo$_{80}$O$_{23}$, 500$-$620°C for monoclinic Mo$_{4}$O$_{11}$, 600$-$780°C for monoclinic Mo$_{9}$O$_{26}$ and 750$-$780°C for triclinic Mo$_{9}$O$_{26}$. Formation temperature of single crystals of each phase was the same. The photographs of some typical crystals are shown in Fig. 1$-$8. Single crystals of MoO$_2$ were polyhedral and about 2 mm in size, as shown in Fig. 1. Single crystals of Mo$_4$O$_{11}$ shown in Fig. 2 and 3 were thin plate like with well-developed crystal face of (100). Developed crystal face of single crystal is (010) plane for Mo$_8$O$_{23}$ (monoclinic) and monoclinic Mo$_9$O$_{26}$. Single crystals of triclinic Mo$_9$O$_{26}$ were simultaneously grown at source zone and crystallization zone, as shown in Fig. 6 and 7 because temperature difference between the source zone and the crystallization zone was very small. Transport of
Crystal Growth of Molybdenum Oxides

Fig. 5  Triclinic Mo$_9$O$_{26}$ crystals

Fig. 6  Monoclinic Mo$_9$O$_{26}$ crystals grown at crystallization zone

Fig. 7  Monoclinic Mo$_9$O$_{26}$ crystals grown at source zone

Fig. 8  MoO$_3$ crystals

Fig. 9  Electrical resistivity-temperature curves of Mo$_9$O$_{26-1}$ single crystals
MoO₃ occurred without transport agent TeCl₄. This may be due to vaporization of MoO₃. The value of transport rate of MoO₃ in Table I shows the subtraction of the data due to vaporization of MoO₃ from the experimental data using TeCl₄.

Electrical resistivities of as-grown single crystals were measured from liquid nitrogen temperature to room temperature. Figure 9 shows the results of the electrical resistivity measurement. Intermediate oxides except triclinic Mo₉O₂₆ were suggested to be metallic conductive in consideration of the value and the temperature dependence of resistivity. Triclinic Mo₉O₂₆ showed semiconduction with the activation energy of 0.29 eV.

REFERENCES