

## Crystal Growth of Molybdenum Oxides by Chemical Transport

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Single crystals of  $\text{MoO}_2$ ,  $\text{MoO}_3$ , and  $\text{Mo}_n\text{O}_{3n-1}$  ( $n=4, 8, 9$ ) were grown by chemical transport using  $\text{TeCl}_4$  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  $\text{Mo}_n\text{O}_{3n-1}$  between  $\text{MoO}_2$  and  $\text{MoO}_3$ . The phase diagram of the Mo-O system<sup>1)</sup> showed that there are two distinct oxides,  $\text{Mo}_4\text{O}_{11}$  and  $\text{Mo}_9\text{O}_{26}$  between  $\text{MoO}_2$  and  $\text{MoO}_3$ . Kihlberg<sup>2)</sup> recognized five compounds as the intermediate oxides ( $\text{Mo}_n\text{O}_{3n-1}$ ), that is,  $\text{Mo}_4\text{O}_{11}$ ,  $\text{Mo}_5\text{O}_{14}$ ,  $\text{Mo}_8\text{O}_{23}$ ,  $\text{Mo}_9\text{O}_{26}$ , and  $\text{Mo}_{13}\text{O}_{38}$ , of which  $\text{Mo}_4\text{O}_{11}$  and  $\text{Mo}_9\text{O}_{26}$  are dimorphic. These intermediate oxides are the Magneli phases whose crystal structures can be described on the basis of the  $\text{ReO}_3$  type.<sup>2)</sup>

Chemical transport in the closed system has been applied to the growth of single crystal of the Magneli phases ( $\text{V}_n\text{O}_{2n-1}$ ,  $\text{Ti}_n\text{O}_{2n-1}$ ) using  $\text{TeCl}_4$  as transport agent.<sup>4~9)</sup> 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<sup>4~7)</sup> recently succeeded in growing single crystals of  $\text{V}_n\text{O}_{2n-1}$  and  $\text{Ti}_n\text{O}_{2n-1}$  by the chemical transport which had no need of the procedure of pressure control. The phase of single crystals ( $\text{V}_n\text{O}_{2n-1}$ ) obtained by this method was all the same as that of source material. Therefore, it was considered that the single crystals of  $\text{Mo}_n\text{O}_{3n-1}$  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 dioxide and trioxide. Mixtures of  $\text{MoO}_3$  and  $\text{MoO}_2$  (3:1 in mole ratio) were pressed and placed in evacuated silica tube. The sealed tubes were heated at  $550^\circ\text{C}$  for 14 days in preparation of monoclinic  $\text{Mo}_4\text{O}_{11}$  and at  $650^\circ\text{C}$  for 5 days in preparation of orthorhombic  $\text{Mo}_4\text{O}_{11}$ .

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The products were confirmed as a single phase by X-ray diffraction. Powders of  $\text{Mo}_8\text{O}_{23}$  and  $\text{Mo}_9\text{O}_{26}$  were prepared from  $\text{MoO}_3$  and  $\text{Mo}_4\text{O}_{11}$ . The sealed tubes containing the mixture of  $\text{MoO}_3$  and  $\text{Mo}_4\text{O}_{11}$  (4:1 in mole ratio) were heated at  $700^\circ\text{C}$  for 3 days in preparation of  $\text{Mo}_8\text{O}_{23}$ . The mixtures of  $\text{MoO}_3$  and  $\text{Mo}_4\text{O}_{11}$  (5:1 in mole ratio) in the sealed tube were heated at  $750^\circ\text{C}$  for 2 days to product monoclinic  $\text{Mo}_9\text{O}_{26}$  and at  $700^\circ\text{C}$  for 3 days to product triclinic  $\text{Mo}_9\text{O}_{26}$ . 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.  $\text{TeCl}_4$  powder was added as transport agent into the silica tube. This procedure performed in a dry box to prevent  $\text{TeCl}_4$  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.

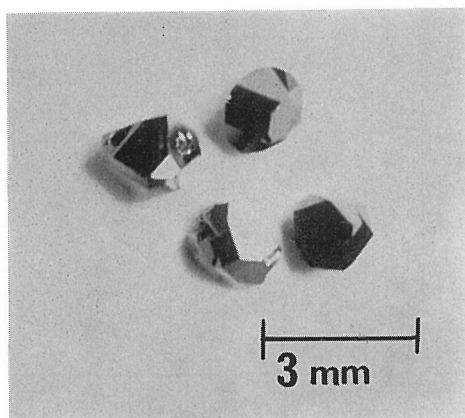
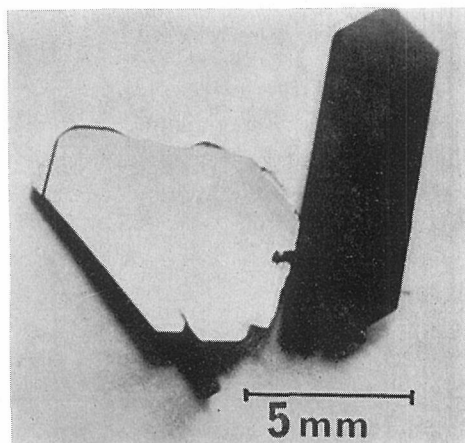
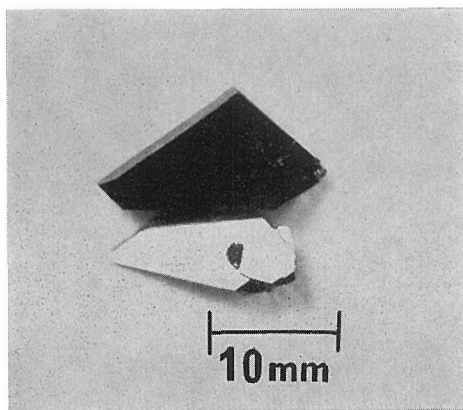
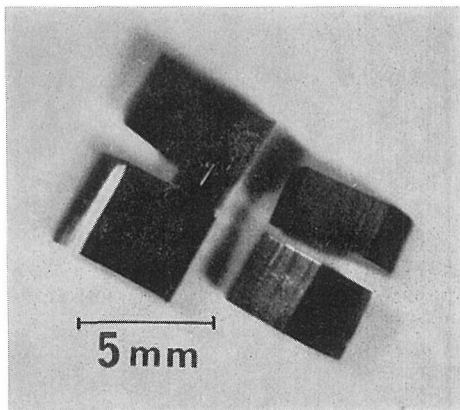
### III RESULTS

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

Table I

| Source materials<br>(2 grams)            | Temperature gradient<br>(deg/degC) | $\text{TeCl}_4$<br>(mg/cc) | Transport time<br>(hr) | Transport rate<br>(mg/hr) | Transported material                     | comment                   |
|------------------------------------------|------------------------------------|----------------------------|------------------------|---------------------------|------------------------------------------|---------------------------|
| $\text{MoO}_2$                           | 700/630                            | 3.0                        | 70                     | 10.3                      | $\text{MoO}_2$                           | reddish purple polyhedral |
| $\text{Mo}_4\text{O}_{11}$<br>(ortho.)   | 690/640                            | 3.0                        | 70                     | 26.4                      | $\text{Mo}_4\text{O}_{11}$<br>(ortho.)   | royal purple thin plate   |
| $\text{Mo}_4\text{O}_{11}$<br>(ortho.)   | 650/560                            | 3.0                        | 50                     | 31.0                      | $\text{Mo}_4\text{O}_{11}$<br>(monocli.) | royal purple thin plate   |
| $\text{Mo}_4\text{O}_{11}$<br>(monocli.) | 580/500                            | 3.0                        | 50                     | 26.6                      | $\text{Mo}_4\text{O}_{11}$<br>(monocli.) | royal purple thin plate   |
| $\text{Mo}_8\text{O}_{23}$               | 750/730                            | 0.5                        | 71                     | 8.8                       | $\text{Mo}_8\text{O}_{23}$               | purplish black            |
| $\text{Mo}_9\text{O}_{26}$<br>(monocli.) | 770/760                            | 0.5                        | 69                     | 6.1                       | $\text{Mo}_9\text{O}_{26}$<br>(monocli.) | black                     |
| $\text{Mo}_9\text{O}_{26}$<br>(monocli.) | 770/745                            | 0.5                        | 70                     | 16.7                      | $\text{Mo}_9\text{O}_{26}$<br>(tricli.)  | black needle              |
| $\text{Mo}_9\text{O}_{26}$<br>(tricli.)  | 750/730                            | 0.5                        | 70                     | 13.8                      | $\text{Mo}_9\text{O}_{26}$<br>(tricli.)  | black needle              |
| $\text{MoO}_3$                           | 650/600                            | 3.0                        | 74                     | 11.9                      | $\text{MoO}_3$                           | light yellow needle       |

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  $\text{Mo}_4\text{O}_{11}$  and  $\text{Mo}_9\text{O}_{26}$  depended on the temperature of the crystallization zone, independently of the phase of source material. It was reported by Kihlberg<sup>2)</sup> that the formation temperature by solid state reaction is  $620\sim 680^\circ\text{C}$  for orthorhombic  $\text{Mo}_4\text{O}_{11}$ ,  $500\sim 620^\circ\text{C}$  for monoclinic  $\text{Mo}_4\text{O}_{11}$ ,  $600\sim 780^\circ\text{C}$  for monoclinic  $\text{Mo}_9\text{O}_{26}$  and  $750\sim 780^\circ\text{C}$  for triclinic  $\text{Mo}_9\text{O}_{26}$ . 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  $\text{MoO}_2$  were polyhedral and about 2 mm in size, as shown in Fig. 1. Single crystals of  $\text{Mo}_4\text{O}_{11}$  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  $\text{Mo}_8\text{O}_{23}$  (monoclinic) and monoclinic  $\text{Mo}_9\text{O}_{26}$ . Single crystals of triclinic  $\text{Mo}_9\text{O}_{26}$  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

Fig. 1  $\text{MoO}_2$  crystalsFig. 2 Monoclinic  $\text{Mo}_4\text{O}_{11}$  crystalsFig. 3 Orthorhombic  $\text{Mo}_4\text{O}_{11}$  crystalsFig. 4  $\text{Mo}_8\text{O}_{23}$  crystals

# Crystal Growth of Molybdenum Oxides

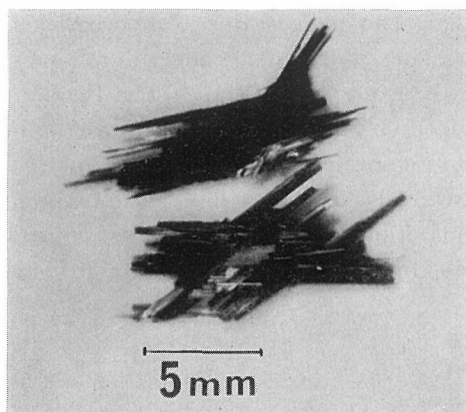


Fig. 5 Triclinic  $\text{Mo}_9\text{O}_{26}$  crystals

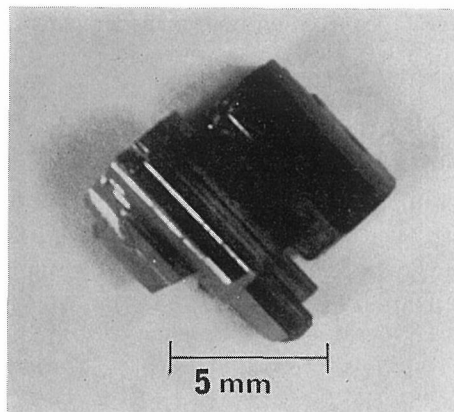


Fig. 6 Monoclinic  $\text{Mo}_9\text{O}_{26}$  crystals grown at crystallization zone

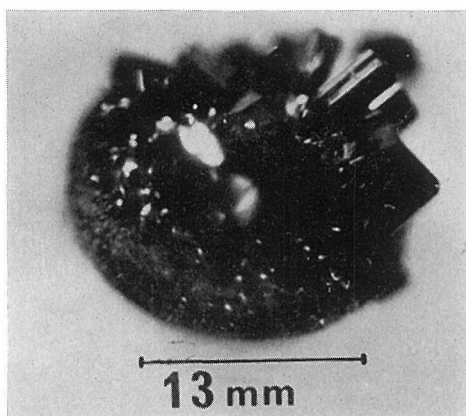


Fig. 7 Monoclinic  $\text{Mo}_9\text{O}_{26}$  crystals grown at source zone

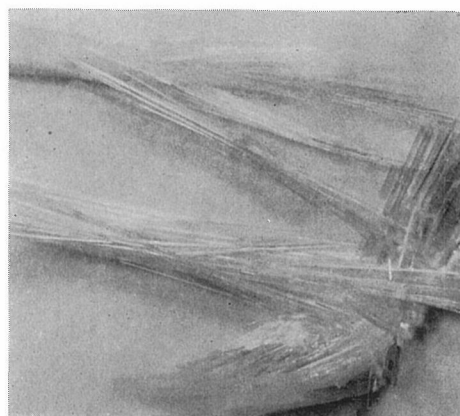


Fig. 8  $\text{MoO}_3$  crystals

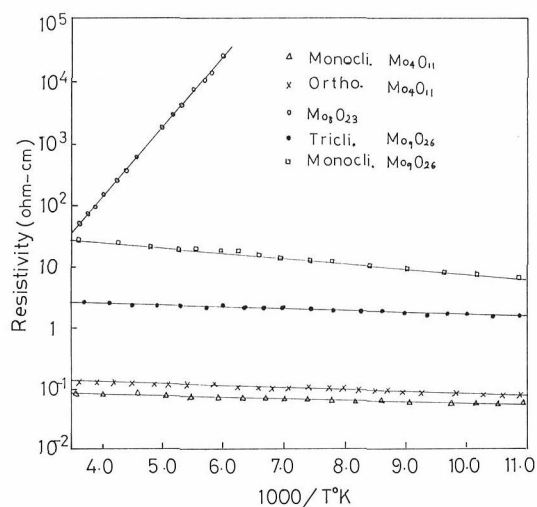


Fig. 9 Electrical resistivity-temperature curves of  $\text{Mo}_n\text{O}_{3n-1}$  single crystals

$\text{MoO}_3$  occurred without transport agent  $\text{TeCl}_4$ . This may be due to vaporization of  $\text{MoO}_3$ . The value of transport rate of  $\text{MoO}_3$  in Table I shows the subtraction of the data due to vaporization of  $\text{MoO}_3$  from the experimental data using  $\text{TeCl}_4$ .

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  $\text{Mo}_9\text{O}_{26}$  were suggested to be metallic conductive in consideration of the value and the temperature dependence of resistivity. Triclinic  $\text{Mo}_9\text{O}_{26}$  showed semiconduction with the activation energy of 0.29 eV.

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