

Crystal growth of barium molybdate by flux evaporation

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Abstract. Single crystals of BaMoO_4 have been grown by isothermal evaporation of lithium chloride at 700°C . The morphology and mechanism of growth of the crystals have been discussed. The quality of the crystal has been assessed by selective etching.

Keywords. Barium molybdate; flux evaporation; morphology; growth mechanism; etching.

1. Introduction

Barium molybdate belongs to an interesting (morphotropic and isostructural) series of Scheelite-type crystals of space group C_{4h}^{64} or $I_{41/a}$ (Wyckoff 1951) and finds wide applications in optics, acoustics and electronics. Crystals of BaMoO_4 have been grown by hydrothermal (Litvin *et al* 1966), pulling (Tu chen 1973) and gel (Cho *et al* 1977) methods, but with limited success. Packter and Roy (1971, 1975) reported crystallization studies of BaMoO_4 precipitates from lithium chloride melts but were not concerned with the size and purity of their products. This paper reports attempts to grow larger and better single crystals of BaMoO_4 by flux evaporation method and investigate their growth characteristics.

2. Experimental and observations

2.1 *Equipment and materials*

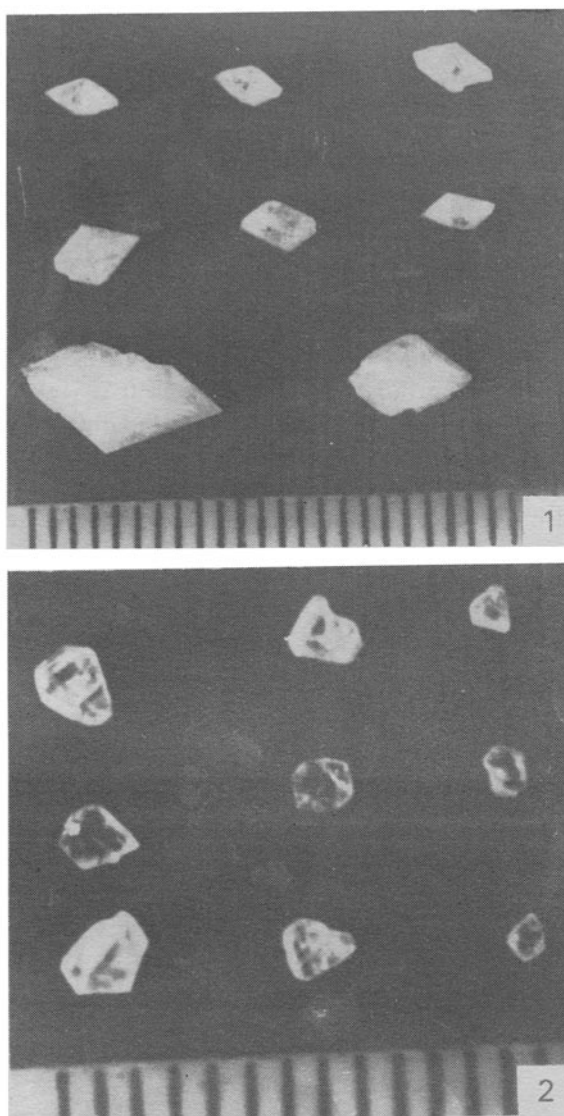
A vertical-tube muffle furnace was constructed with cylindrical alumina muffle wound by super kanthal heating element and covered by insulating bricks and lining. A stabilized power of 1.5 kW was used. A 25 ml platinum crucible of 0.5 mm wall thickness was employed to contain the growth charge. The temperatures were monitored by Pt-Pt/10% Rh thermocouple placed just below the crucible.

The chemicals used in the present study were : Sendz Swijur BaMoO_4 powder of 99.6% purity and SD's reagent grade hydrated LiCl.

2.2 *Flux growth*

To induce supersaturation in the high temperature solution to onset free crystallization, (Roy 1966; Wood and White 1968; Webster and White 1969),

isothermal solvent evaporation was preferred to slow cooling procedure. The results of different growth experiments (keeping the soak temperature of 700°C) carried out using different compositions and soak periods are shown in table 1. The quantities of initial materials were properly weighed, mixed thoroughly using a pestle and mortar and then packed into the crucible provided with a loosely fitting platinum lid. The charged crucible was placed in the furnace and the power turned on to bring a temperature of 750°C . The mixture was heated at this temperature, which was 50°C higher than the soak temperature, for about 30 min to ensure complete



Figures 1-2. (scale: 1 div = 1 mm) **1.** A few bipyramidal crystals of BaMoO_4 . **2.** Thin, platy crystals of BaMoO_4 .

solution in the crucible. The temperature was then rapidly lowered to the soak temperature of 700°C and maintained for prolonged periods as specified in table 1, thus allowing solvent evaporation to take place. Consequently, the crystal growth occurred at 700°C. At the end of the soak periods, uniform cooling at the rate of 10°C hr⁻¹ was carried out down to 500°C with a view to avoiding charge eruptions in the crucible. The furnace power was then put off and the crucible allowed to cool down to room temperature overnight. The contents of the crucible were then leached with hot distilled water which easily separated the insoluble crystals from the matrix of the solidified charge.

3. Characterization

3.1 Crystal habits and properties

Many good crystals of BaMoO₄ of about 11 mm size, together with a number of smaller ones, were obtained. This size is, as usually expected, less than that of pulled crystals (TuChen1973) but is indeed greater than others reported in literature (Litvin *et al* 1966; Cho *et al* 1977; Packter and Roy 1971, 1975). Figure 1 shows some typical well-developed bipyramidal BaMoO₄ crystals, while figure 2 shows thin, transparent plates.

The crystal perfection was found to be dependent on soak period, while the crystal morphology was sensitive to the flux-to-solute ratio, as revealed by table 1. Using the charge composition, as in the experiment 1(a, b) in table 1, bipyramidal crystals bounded by (011) faces were obtained, and a variation, particularly in respect of size and degree of transparency, with soaking time was observed. Another composition, in the experiment 2(a, b) in table 1, yielded thin, transparent platy crystals by 12 hr of evaporation. And, the same charge resulted hopper crystals with spiral-like terraced depressions by 22 hr of isothermal soaking.

The lattice parameters of the grown crystals were determined by x-ray diffraction techniques, which matched well with the literature values (Powder data file 1967). Some of the characteristics examined have been listed in table 2.

Table 1. Correlation of crystal morphology, size and quality with growth parameters (Soak temperature : 700°C)

Sl. No.	Composition of starting materials	Soak time (hrs)	Results
1(a)	10 g BaMoO ₄ + 7.1 g LiCl, H ₂ O	12	Transparent, bipyramidal crystals, up to 1 mm across
(b)	Same as (a)	50	Smoky and distorted bipyramidal crystals up to 11 mm across
2(a)	10 g BaMoO ₄ + 5.0 g LiCl, H ₂ O	12	Thin, transparent platy crystals
(b)	Same as (a)	22	Milky, hopper crystals.

Table 2. Some characteristic properties of BaMoO₄ crystals.

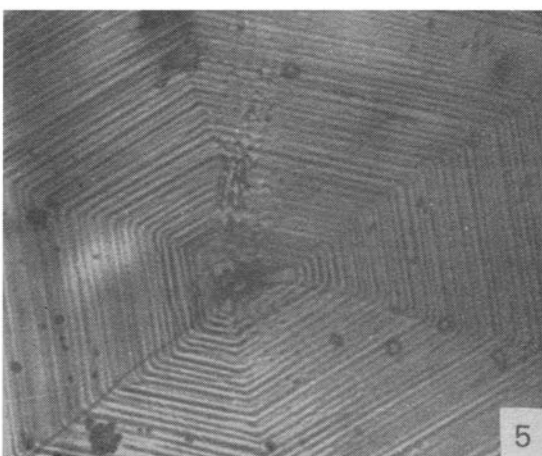
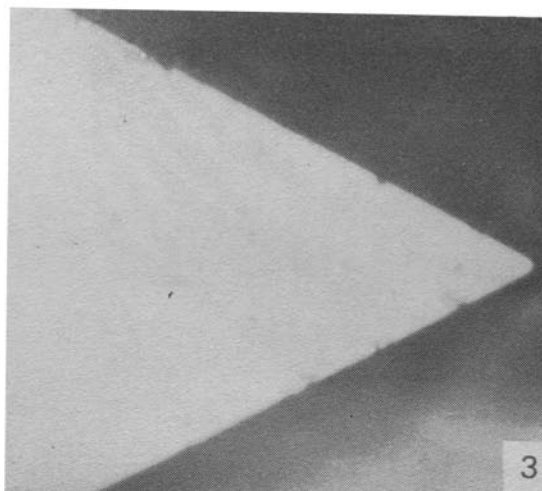
Properties studied	BaMoO ₄
Maximum size obtained	11 mm
Colour	Transparent to opaque
Habit	Tetragonal bipyramidal
Unit cell dimensions	$a = b = 5.58 \text{ \AA}$ $c = 12.79 \text{ \AA}$
Average microhardness on (011) plane	3.55 mohs
Pycnometer density	4.9 g ml ⁻¹
Cleavage	(001)
Estimated dislocation density	$2 \times 10^3 \text{ cm}^{-2}$
Dielectric constant parallel to c-axis at room temperature (35°C) and at 10 ² Hz	62.55
DC conductivity at room temperature (35°C)	$1.95 \times 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$

3.2 Microtopographical characteristics

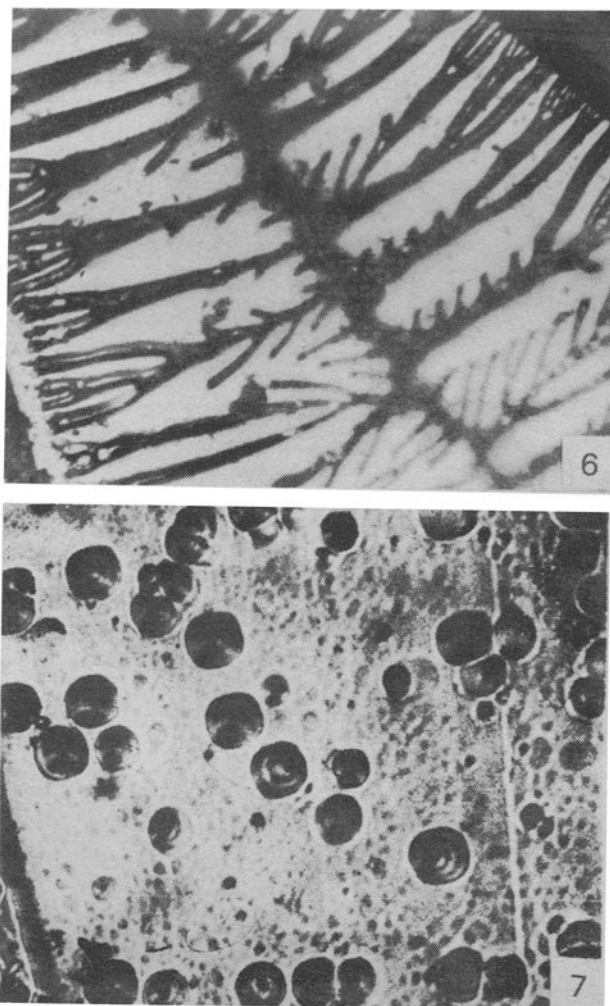
The mechanism of crystal growth may, in general, be understood by either x-ray topography of sections through crystals (Authier 1972), measurement of growth rate as a function of supersaturation (Elwell and Dawson 1972) or observing the surface features. The as-grown (011) faces of the smaller (up to 1 mm size) crystals examined in the 'Epignost' optical microscope were found smooth and flat (figure 3) indicating that the mechanism of two-dimensional spreading and piling of growth layers across the crystal face is responsible for the growth of these crystals. This mechanism is supported by the complete absence of growth spirals on habit faces and by the movement of growth layers (figure 4) originated from the edges and corners. In fact, the sites of initiation of growth layers exist due to transport of solute by diffusion onto a growing crystal, thus creating a relatively higher supersaturation near the edges and corners of the crystals than in the middle (Chase 1968). The stability of the plane interface is to be interrupted by edge nucleation only, and the subsequent increase in supersaturation gradient leads to characteristic terraced depressions, as shown in figure 5, which probably arise as a result of propagation of densely packed lamellar sheets across the growing face. In the final stage of growth, due to the prevalent high degree of supersaturation and instability of the last layer of free surface, dendritic precipitation occurs on the faces. Most of the larger crystals (≥ 1 mm size) obtained exhibit typical dendritic patterns such as those shown in figure 6.

3.3 Etching

The dislocation density in the grown crystals was determined by selective etch pits count on the only (001) cleavage face, employing 10% nitric acid solution as an etchant. The average dislocation density of 2×10^3 pits cm⁻² reveals reasonable



Figures 3-5. 3. A typical smooth and flat habit face of BaMoO₄ crystal. 4. Layers originating from edges and corners of the grown faces. 5. Spiral-like terraced depression on the grown face. (3, 4. × 180, 5. × 225).



Figures 6–7. 6. Typical growth dendrites on the as-grown (011) face. 7. An etch pit pattern on (001) cleavage plane. (6. $\times 180$, 7. $\times 450$).

perfection of the crystals and absence of low angle tilt-twist boundaries. A typical etch pattern on a cleavage face is displayed in figure 7.

4. Conclusions

Single crystals of barium molybdate are grown by isothermal evaporation of lithium chloride flux. Crystal morphology, size and quality are sensitive to the composition of the starting material and soak times. The observed microstructures indicate that the screw dislocation mechanism may not operate in these crystals; the crystals possibly grow by the mechanism of two-dimensional nucleation and propagation

of growth layers. The crystals are better, both in respect of size and quality, than those obtained by hydrothermal and other flux methods.

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References

- Authier A 1972 *J. Cryst. Growth* **13/14** 34
Chase A B 1968 *J. Am. Ceram. Soc.* **51** 567
Cho S A, Gomez J A, Camisothi R and Ohep J C 1977 *J. Mater. Sci.* **12** 816.
Elwell D and Dawson R 1972 *J. Cryst. Growth* **13/14** 555
Lityin B N, Dem'yanets L N and Garshina L S 1966 *Growth of crystals* (eds) A V Shubnikov and N N Sheftal (New York: Consultants Bureau) Vol. **4** p. 134.
Packter A and Roy B N 1971 *Kristall. Tech.* **6** 39
Packter A and Roy B N 1975 *Kristall. Tech.* **10** 383
Powder Data File 1967 American Society for Testing Materials, Philadelphia, Pennsylvania, Card Number 8-455
Roy R 1966 *Mater. Res. Bull.* **1** 299
Tu Chen 1973 *J. Cryst. Growth* **20** 29
Webster F W and White E A D 1969 *J. Cryst. Growth* **5** 167
Wood J D C and White E A D 1968 *J. Cryst. Growth* **3/4** 480
Wyckoff R W G 1951 *Crystal structures* (New York: Interscience)