THE AMERICAN MINERALOGIST, VOL. 52, JULY–AUGUST, 1967

GROWTH OF BROMELLITE CRYSTALS

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INTRODUCTION

During an investigation of flux growth of bromellite crystals, variations of crystal morphology were found which were dependent only upon the flux composition. Two morphologies were found, a rod-shaped crystal with an external *c*/*a* ratio up to 50 and a prismatic crystal with a *c*/*a* ratio of about 1 to 2. The flux system explored was Na_2O-B_2O_3. This solvent was chosen because it has much higher solubilities at 1250°C for BeO than the molybdate and lead fluxes (Newkirk, 1965; Austerman, 1962; Linares, 1962), *e.g.*, 20 as opposed to 5 weight percent.

CRYSTAL GROWTH

The crystal growth experiments were performed as described previously (Linares, 1962). The conditions and the morphology obtained are given in Table 1. In the Na_2O-B_2O_3 system, prismatic BeO crystals are formed at Na/B ratios of 1. These crystals (Fig. 1) show the typical [0001] polarity previously observed (Austerman, 1962). As the B_2O_3 content is raised to a Na/B ratio of 0.5, the rod form appears. The two forms were never found together in a run indicating that flux composition was responsible for the change rather than temperature or a change in nucleation.

In the experiments just described, the cooling rate of the melts was from 1 to 5°C per hour. When the cooling rate was increased to 25°C per hour, with Na/B = 0.5, crystals of BeO formed which were hollow on one end (Fig. 2). If the cooling rate is increased to 50°C/hr., the edges of the tube become disconnected (Fig. 3). At this point, the crystals appear to

TABLE 1. CONDITIONS OF GROWTH OF BROMELLITE CRYSTALS

All grown at 1250–900°C

Weight BeO, gr	Weight flux, gr	Cooling rate °C/hr.	Morphology
9.5	50 $NaBO_2$	1–5°	Prismatic
9.5	50 $Na_2B_4O_7$	1–5°	Rods
9.5	50 $Na_2B_4O_7$	25°	Hollow rods
9.5	50 $Na_2B_4O_7$	50°	Disconnected ends on hollow rods
9.5	50 $Na_2B_4O_7$	100°	Whiskers

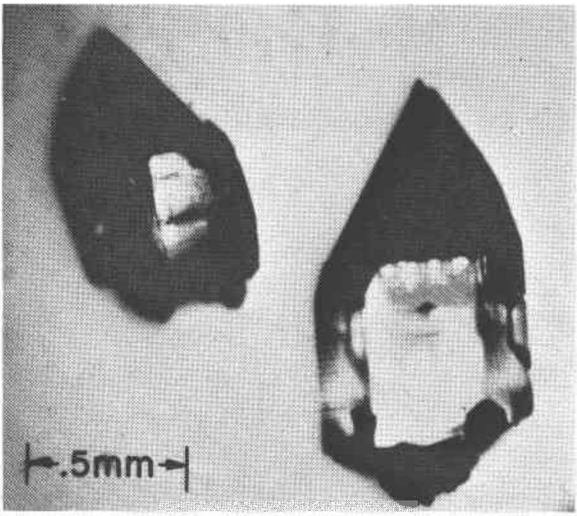

FIG. 1. BeO rhombohedrons.

have been formed by dendritic growth. Increasing the cooling rate to 100°C/hr. results in the formation of whiskers (Fig. 4). These vary from 10 to 50 μ in diameter and up to 1 cm or more in length.

If crystal growth kinetics are strictly controlled by supersaturation, the growth rate will be a function of cooling rate. When a point is reached

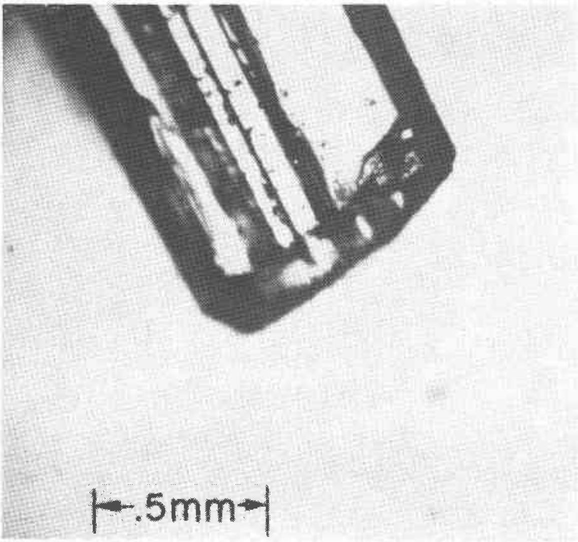

FIG. 2. hollow BeO rods.

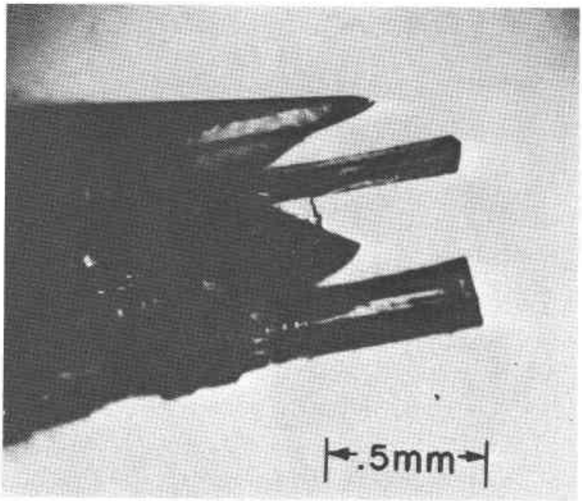

FIG. 3. Hollow BeO rods with break up of growth on ends.

such that growth rate is constant even with increased cooling, then the process is diffusion limited, since in diffusion-limited situations the diffusion rate and not supersaturation determines the growth kinetics. In systems where Na/B$=0.5$ we find that the *c* axis growth is indeed linear with growth rate; however, the *a* axis growth, as measured by the thickness of the walls of the hollow crystals and the diameter of whiskers, is a constant. With flux ratios of 1, the *c* axis and *a* axis growth rates are constant with time, and the *a* axis rate is the same as that for flux ratios of 0.5. Thus, the habit change can be attributed to a change of the rate controlling mechanism on the *c* axis from diffusion controlled to super-

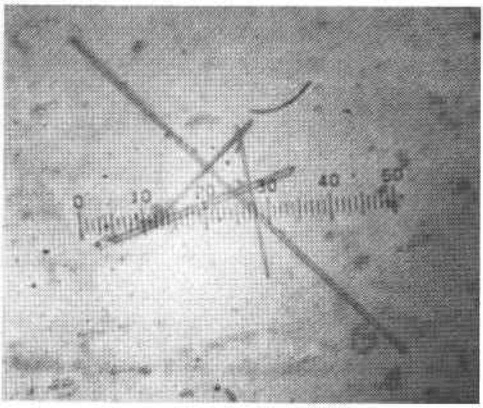

FIG. 4. BeO whiskers (scale 13 microns/division).

saturation controlled. This is evidently regulated by the amount of boron oxide in the flux which influences certain growing faces depending on its concentration. It has also been observed that the viscosity increases as Na/B decreases. While high viscosity is usually associated with a low diffusion rate, it would not necessarily decrease it preferentially for a particular crystal direction. It does not seem likely therefore that viscosity could control the morphology especially since Newkirk and Smith (1965) observe changes in morphology in lithium molybdate flux with boron oxide additions which are far too small to significantly affect viscosity.

It is not clear why the hollow rods form, however, this shape has a high surface area which can use the large amount of BeO available for deposit. It would appear that at higher cooling rates (50°C/hr.), the supersaturation is so high that even the hollow geometry cannot accommodate all the material available for deposition, and the walls begin to break up, thereby further increasing their surface area. At still higher rates (100°C/hr.) this break-up is complete and crystals grow as individual filaments.

ACKNOWLEDGMENTS

The author would like to thank J. B. Schroeder and J. F. Nester for many valuable discussions during the course of this study.

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THE AMERICAN MINERALOGIST, VOL. 52, JULY–AUGUST, 1967

COCINERITE DISCREDITED[1]

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In 1901, during a brief reopening of the centuries-old Cocinera Mine, at Ramos, San Luis Potosi, Mexico, a large pocket of oxidized ore was encountered near the bottom of the mine, at a depth of 1100 feet. This ore was reported to have been a complex mixture of "the red and black oxides of copper, some carbonates and some metallic copper and metallic silver" (Hough, 1919), and to contain a few pounds of an unknown metallic mineral. Pieces of this unknown mineral were analyzed by the chemist of the Mexican Copper Company, owners of the mine at the time of the

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[1] Publication is authorized by the Director, U. S. Geological Survey.