

STUDIES ON THE FORMATION OF CRYSTALLINE
SYNTHETIC BROMELLITE. II. MACROCRYSTALS¹

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ABSTRACT

Synthetic bromellite (BeO) macrocrystals grown from molten lead oxide, lead fluoride, and their equimolar mixtures using slow cooling techniques are nearly always prismatic with one end terminated by a small pyramid. Crystals grown from molten alkali vanadates, molybdates, and tungstates using a modified Krüger-Fincke method have essentially four basic habits, *i.e.*, platy, prismatic, hemi-pyramidal, and dendritic, although intermediate developments also were observed. The important parameter determining whether a crystal will be either a plate (length/width < 0.81) or a prism (length/width > 0.81) is the temperature. Supersaturation has a smaller, nonsystematic effect on habit control, and is important in regulating nucleation phenomenon and growth rates. Pyramids (length/width $= 0.81$) and dendritic forms (length/width $\gg 0.81$) are rare and occur under rather narrow conditions of temperature and/or supersaturation. Growth habit relationships and positions of nucleation zones were sensitive to the presence of small concentrations of impurities, particularly tetrahedrally coordinating cations with ionic radii $< 0.38 \text{ \AA}$. The pattern of habit change from plates \rightarrow prisms \rightarrow pyramids, as the temperature changes from 1400 to 1000°C, was rationalized in terms of a surface diffusion mechanism similar to the one proposed for habit control in ice, but calculations of nucleation rates suggest that a nucleation phenomenon may also be important, particularly at high supersaturations. The techniques are described for growing large, high-quality crystals from molten lithium molybdate fluxes. Growth rates measured normal to basal surfaces as a function of temperature indicate that the enlargement process in molten lithium dimolybdate requires an activation energy of 15 kcal/mole. Overgrowth on BeO single crystals and on orientated, polycrystalline substrates suggests that nucleation occurs at surface impurities and growth proceeds along the preferential directions $[00 \cdot 1]^*$ and $[11 \cdot 0]^*$.

High-quality crystals, 1.5 cm in length, have been obtained within 24 hours by hydrolyzing BeF_3 vapor in air at 1000° C. The high growth rates results in a somewhat more complex morphology than in other methods, but the crystals are still dominantly prismatic. Crystals obtained from hydrothermal experiments using 2-N NaOH solutions at 420-400° C and 2000 bars are in general of highest quality although much smaller in size and purity. All crystals show essentially the same prismatic habit.

Twinning which could be initiated by selective impurities was commonly observed in all the environments studied and obeys one twin law with $(00 \cdot 1)$ or $(00 \cdot \bar{1})$ as the twin plane. The relationships of the structure across the twin boundaries for the two types of twins observed, contact and penetration, are discussed in detail. Etching studies, x-ray diffraction topography, and optical microscopy of penetration twins show the important imperfections to be screw dislocations with $[00 \cdot 1]^*$ Burgers vectors in the central core. These data permitted the growth of penetration type twins to be rationalized in terms of the simultaneous operation of a classical screw dislocation and twin boundary mechanism.

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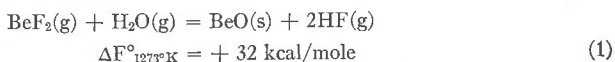
INTRODUCTION

This is the second in a series of two papers dealing with the synthesis of crystalline synthetic bromellite (BeO). In this paper we summarize our observations on the growth of macrocrystals, *i.e.*, high-quality polyhedral and dendritic crystals approaching 1 cm on an edge.

Macrocrystals have been successfully grown by essentially three different methods; crystallization from molten salt solvents, hydrothermal synthesis and vapor phase deposition-decomposition reactions. The molten salt solvents used were those which form simple eutectic systems with BeO and possess high temperature coefficients of solubility—namely, lead oxide, lead fluoride, mixtures of these two compounds, and the alkali vanadates, molybdates, and tungstates. The various aspects of the nucleation and growth were studied in some detail and many data were collected on the physical chemistry of the systems employed. Problems such as the control of the many habits reported (Levin, Rynders, and Dzimian, 1952; Bárta and Bauer, 1957; Linares, 1962; Grimes *et al.*, 1962; Austerman, 1963) to yield desired shapes and attainment of growth conditions which minimize the inclusion and artifacts and yet maximize growth rates have been solved.

PHYSICAL CHEMISTRY OF SOLVENT SYSTEMS

Solubility data have been obtained for the various molten fluxes, and in NaOH solutions, by determining the loss in weight of a polycrystalline BeO bar immersed in the solvent at a specified temperature and pressure. Generally 8 h were sufficient to saturate the molten salts, but NaOH solutions were heated for a minimum of 24 h. The solubility of BeO in various NaOH solutions was studied in the pressure range 1000–4000 bars. Values of solubility are believed reliable to 5% in the case of molten salt solvents and to 0.5% for hydrothermal solvents. Phase relationships in the various molten salt solvents were constructed from solubility data and from cooling curves. In the case of the Na₂O-BeO-H₂O system, the univariant pressure-temperature curve was constructed from data obtained by treating finely powdered BeO or Be(OH)₂ under identical conditions to those in the solubility experiments and to pressures as low as 100 bars. Studies were not conducted on the reaction



in view of the comprehensive work reported by Ozhigan and Zatsorin (1961). A compilation of all the solubility data and the phase diagrams constructed are available from the authors on request (Newkirk and

Smith, 1963). Some of the more important results, however, are discussed below.

Molten salt solvents. Figure 1(a-b) shows the linear dependence of BeO solubility on temperature in PbO and in PbO-PbF₂ fluxes, respectively. As the data indicates, the solubility of BeO in PbO is low but can be increased ten fold at 1000° C, for example, by the addition of an equimolar

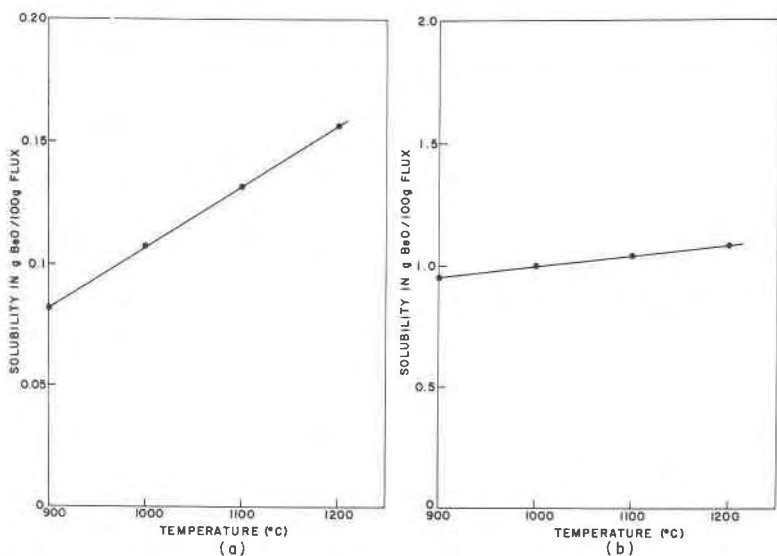


FIG. 1. Dependence of BeO solubility on temperature in (a) PbO fluxes, and in (b) 50 m/o PbO-50 m/o PbF₂ fluxes.

quantity of PbF₂. At constant temperature, the BeO solubility was found to increase linearly with increasing PbF₂ concentrations. The PbO and PbO-PbF₂ flux compositions form excellent low melting systems in which to carry out BeO crystal growth, but the high vapor pressure and corrosive nature of these fluxes limit their use to rather low operating temperatures.

In the case of the alkali molybdates, tungstates, and vanadates, the BeO solubility is generally much higher and depends on the temperature and/or the flux composition. This solution phenomenon is a fortunate circumstance, since both temperature and supersaturation can be independently controlled. An example is illustrated in Fig. 2(a, b) for the particular case of the system Li₂MoO₄-MoO₃. Figure 2(c) shows the phase relationships which exist in the system BeO-Li₂Mo₂O₇. At constant temperature, the BeO solubility increases linearly with MoO₃ additions

to Li_2MoO_4 until the composition $\text{Li}_2\text{Mo}_2\text{O}_7$ is reached. Further additions of MoO_3 causes the solubility to increase in a nonlinear manner. At constant solubility the relationship between temperature and composition is hyperbolic in nature. In general, the solubility of BeO for a given flux composition increases with increasing temperature in all the systems studied. The dependence on temperature obeys van't Hoff's equation

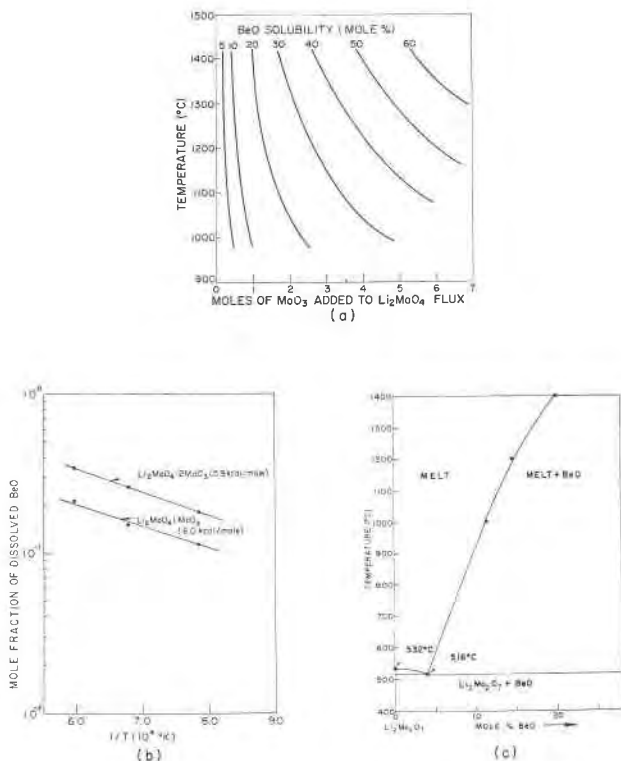


FIG. 2. (a) The relationship between temperature and composition at constant BeO solubility in the system $\text{Li}_2\text{MoO}_4\text{-MoO}_3$. (b) Van't Hoff relationship between BeO solubility and temperature for different compositions in the system $\text{Li}_2\text{MoO}_4\text{-MoO}_3$ and the corresponding calculated heats of solution. (c) Phase relationships in the system $\text{BeO-Li}_2\text{Mo}_2\text{O}_7$. Since the BeO solubility depends on both the temperature and/or $\text{Li}_2\text{MoO}_4\text{-MoO}_3$ composition, both temperature and supersaturation can be controlled independently.

with calculated heats of solution ranging from 6–12 kcal/mole. In general, the BeO solubility decreased for a given flux composition with increasing atomic number of the alkali metal cation and increased in the order vanadates—molybdates—tungstates for a given alkali metal cation at constant temperature. The dependence of BeO solubility on the

concentration of oxide added to the normal flux composition indicates complexing action between the solvent and solute and is consistent with the well-known tendency of these systems to form high molecular weight, polymeric species in the melt (Killeffer and Linz, 1952). In fact, one of the remarkable properties of lithium dimolybdate is that it can be used to grow crystals at 1400° C, above the boiling point of pure MoO₃. The structure of the solute bearing species in the molten flux is still quite speculative, although reasonably stable tungstate complexes have been reported (Chupka *et al.*, 1959) to exist in the gas phase having the general formula, WO_x(BeO)_y, where x = 1, 2, . . . , and y = 1, 2, High temperature infrared absorption spectroscopy and resistance measurements indicate that the species in tungstate and molybdate flux systems lacks a formal static charge but perhaps are polarized, and that the attached BeO does not interfere with the vibrational modes of the polymolybdate or polytungstate ion.

Our observations on the relative stability of pure alkali vanadate, molybdate and tungstate compounds are in agreement with the quantitative measurements of Spitsyn and Kuleshov (1951), which show that as the solubility of BeO decreases, the thermal stability decreases and the volatility of the flux increases. In the more unstable fluxes, reversible reduction of Group V or Group VI cations occurs. This is indicated by (1) a change in the color of the flux from a clear or straw-yellow color to black, (2) a reversal of the normal solubility behavior, and (3) the presence of minute bubbles, homogeneously distributed throughout the flux. In most cases, the color is retained when a sample is withdrawn from the molten flux and rapidly cooled. In some cases, bubbling oxygen through the flux changes the color from black to a light gray or brown, suggesting that some reversal of the reduction process could be accomplished. The effect of bubbling oxygen through the fluxes on the BeO solubility was negligible and was abandoned as a corrective procedure. It is worthwhile to mention that one of the striking features of alkali vanadate fluxes is their facility to creep. A filled 100-ml crucible completely emptied itself in 3 days at 1200° C by this action. This phenomenon played havoc with furnaces and seriously limited application of these compositions to our nucleation and growth studies. Alkali chromates behaved in a similar manner and also prevented their inclusion in the crystal growth studies.

Hydrothermal solvents. In NaOH solvents, the BeO solubility is essentially independent of pressure. Figure 3 a shows the dependence of solubility on NaOH concentration at temperatures to 600° C. The solubility, as shown in Fig. 3b, varies linearly with increasing temperature in a given solvent concentration and, the temperature coefficient of solubility is

reasonably large in all solutions above 1.01-molal NaOH. The dependence on temperature obeys van't Hoff's equation and calculated heat of solutions vary from 2.7 ± 0.5 kcal/mole at the lowest concentration to 9.1 ± 0.5 kcal/mole in the 8.02-molal solution. The strong dependence of solubility on the concentration of NaOH suggests that the important species in solution are beryllate anions formed according to the reaction

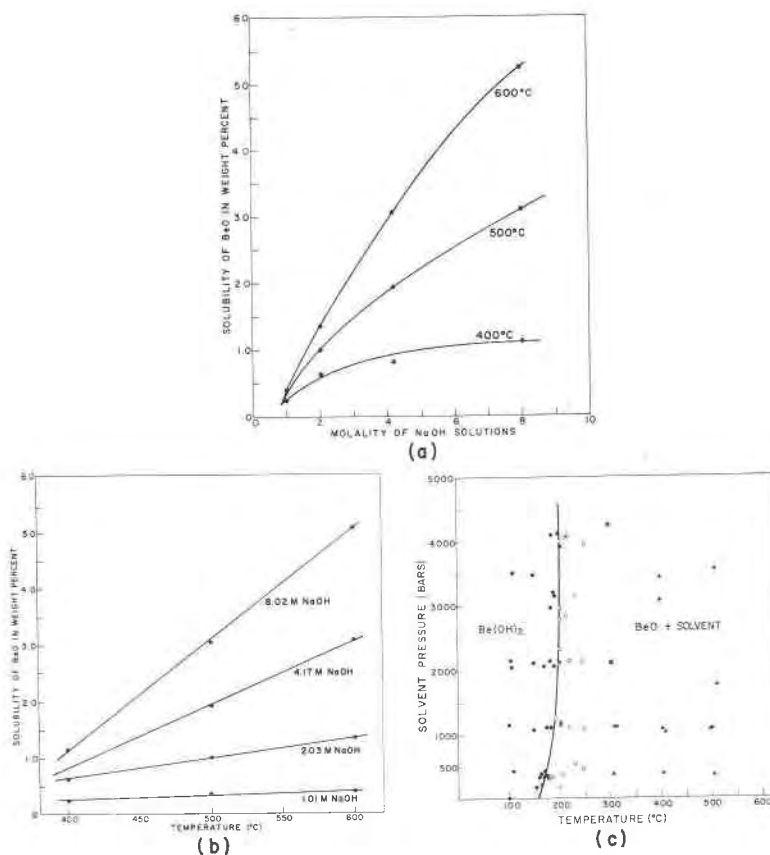


FIG. 3. Dependence of BeO solubility on (a) the concentration of NaOH solutions at different temperatures, and (b) the temperature at different concentrations of NaOH solutions. The solubility is essentially independent of pressure in the range 1000–4000 bars. The phase relationships which exist in the system Na₂O-BeO-H₂O at concentrations of NaOH solutions to 8.02 molal are shown in (c). Filled circles: β -Be(OH)₂. Triangles: well-crystallized BeO. Open circles: BeO with enlarged unit cell. Half-filled circles: BeO with enlarged unit cell and β -Be(OH)₂.

At high $\text{Na}_2\text{O}/\text{BeO}$ ratios, simple anions are probably present, whereas at low $\text{Na}_2\text{O}/\text{BeO}$ ratios, polymeric beryllate anions predominate (Everest *et al.* 1962). The solubility of BeO is much less than found for silica, alumina, and zinc oxide under similar pressure-temperature conditions (Laudise, 1962). As a result one would expect to observe correspondingly lower growth rates. The rate of growth of crystals would undoubtedly be diffusion controlled because of the high viscosity of the concentrated solutions necessary to effect appreciable BeO solubility. Studies of BeO solubility in other hydrothermal solvents are continuing. Figure 3 c shows the p - t diagram for the system $\text{Na}_2\text{O}-\text{BeO}-\text{H}_2\text{O}$ at low concentrations of NaOH . The univariant curve passes through points at $200^\circ\text{C}-4100$ bars and $170^\circ\text{C}-300$ bars. The relationship is similar to that observed in the $\text{BeO}-\text{H}_2\text{O}$ system (Newkirk, 1964). The stability region is well within the capabilities of currently available high pressure equipment. The rather specialized equipment and the techniques involved in studying the nucleation and growth of crystals in various environments are discussed in the following section.

EQUIPMENT AND TECHNIQUES

Crystallization from molten salts. Studies in molten salt environments were carried out either by slow cooling a saturated flux or by transporting BeO along a steady-state thermal gradient (commonly referred to as the modified Krüger-Fincke (1910) method). In slow cooling experiments, 250-ml platinum crucibles, each containing a sintered disc of BeO at the bottom, were filled with the appropriate powdered flux composition. The tightly covered crucibles were heated to maximum temperature, which in some cases was as high as 1200°C , soaked for 8 h, and then cooled at the rate of $4^\circ\text{C}/\text{h}$. The crucibles were withdrawn at the low temperature, the flux poured off, and the crystals leached with an appropriate solvent: hot water in the case of alkali vanadates, molybdates and tungstates and boiling, dilute, nitric acid-acetic acid for PbO and $\text{PbO}-\text{PbF}_2$ mixtures. In the Krüger-Fincke method, the crystal growing composition is held above its liquidus temperature in well-covered 250-ml rectangular platinum trays. The BeO nutrient dissolves in the molten flux and saturates the solution in the upper or hotter part of this system. The saturated solution is then transported by convection to the lower or cooler nucleation zone. In this region, the solution is supersaturated with respect to undissolved BeO , and BeO deposits on the polycrystalline substrates. The cooler, depleted solution returns by convection to the hotter zone, where it dissolves more nutrient and the process is repeated. In both techniques, controlled amounts of impurities are added as the powdered oxide or an easily decomposed salt.

Hydrolysis of BeF₂ vapor. Hydrolysis of BeF₂ vapor was carried out by placing a 50-g charge of BeF₂ powder in a 250-ml platinum container. The container has six equally spaced 0.50-in. diameter holes drilled around its circumference near the top. A loose fitting cover was placed over the container, and the assembly inserted in an electric oven heated in air at 1000° C. After 12 h, crystals were observed to have grown on the platinum cover at the point where vapors evolved to the atmosphere. When possible, controlled impurities were added as the powdered fluoride. When gaseous impurities were used, they were passed through a platinum tube inserted in a hole in the cover and bubbled in the liquid BeF₂.

Hydrothermal methods. Studies in hydrothermal environments were carried out by transporting BeO through NaOH solutions at various temperatures and pressures using a steady-state thermal gradient. The pressure vessels used were of two types, each type designed for a specific upper temperature and pressure limit. The largest vessels, rated for maximum conditions of 500° C and 3000 bars, were fabricated from Timken 17-22A steel and employed a modified Bridgman seal. They were 5.00 in. o.d. × 13.25 in. long and had a cavity 1.25 in. in diameter. The other type of vessels were rated for maximum conditions of 600° C and 4000 bars and were fabricated from Stellite-25. These vessels employed cold-cone closures and were 1.0 in. o.d. × 9.0 in. long with a cavity 0.250 in. in diameter. The nucleation and growth of BeO crystals occurred in a sealed, single-ended silver capsule inserted in the cavity of the pressure vessel. The capsules for the large pressure vessels were threaded on one end to accommodate a cap and had a wall thickness of 0.030 in. and were 10.00 in. long × 0.750 in. i.d. The capsules for the smaller pressure vessels were not threaded and were 3.50 in. long × 0.160 in. i.d. × 0.005 in. wall thickness. The nutrient material, sintered BeO chips, was placed in the bottom of the silver capsule. In the large capsules, directly above the nutrient and attached to a silver rod, is a perforated baffle having an open area of 10%. The baffle divides the capsule into two regions and creates zones of uniform temperature by localizing the temperature differential at the baffle. The upper two-thirds of the capsule is the cooler or nucleation region, and the lower one-third, the hot or solution zone. Coarse-grained, polycrystalline BeO substrates were suspended from hooks attached to the rod framework above the baffle in the nucleation zone. In the smaller capsules, nucleation and growth occurred spontaneously on the walls. The silver capsule was filled to the required fraction of its free volume with NaOH solution and capped. The space between the capsule and the pressure vessel was filled to the same fraction of its free volume and the reactor closed. The silver tube then supported no pressure but satis-

factorily provided an inert container for crystallization. The per cent fill is calculated from P-V-T data for water as determined by Kennedy (Holser and Kennedy, 1958). The vessels were connected to calibrated Bourdon tube gauges and safety devices by a system of valves and fittings. Heating of the larger vessels was accomplished by using two-zone nichrome-wound furnaces hinged on one side about the vertical axis. The temperature of the two zones could be controlled independently to $\pm 2^\circ$ C. Temperatures were measured using six chromel-alumel thermocouples: four strapped to the outside and along the length of the vessel, one inserted in the bottom thermowell, and another penetrating the interior of the vessel through a pressure seal in the top cover. Heating of the smaller vessels was accomplished by single-zone nichrome wound furnaces; natural thermal gradients being sufficient to provide the required temperature differential. In all cases temperatures are believed reliable to $\pm 2^\circ$ C and pressures to $\pm 2\%$. Chemicals were used which were 99.9% pure or better, and all BeO substrates were generally not lower than 94% of theoretical density. Using these equipment and techniques, studies on the nucleation and growth of BeO crystals were routinely carried out in a manner that will now be described.

NUCLEATION AND GROWTH

Molten salt solvents. The nucleation and growth of crystals in alkali vanadate, molybdate, and tungstate systems were studied exclusively by transporting BeO in a steady-state thermal gradient. Conversely, to minimize corrosion of platinum containers, studies in PbO and PbO-PbF₂ mixtures were made exclusively by slow cooling saturated solutions.

In systems employing a steady-state thermal gradient, the important parameter controlling the free energy change which drives the nucleation and subsequent growth of a given crystal habit, is the supersaturation. The level of supersaturation for a given flux composition in the nucleation zone at any nominal furnace temperature is maintained reasonably constant and depends upon the difference (ΔT) of the two temperatures employed. Figure 4(a) shows the dependence of growth rate on undercooling in the case of a variety of lithium molybdate compositions. Generally, undercooling by 5–10° C was insufficient to initiate spontaneous nucleation in molten fluxes. However, once growth started, this level of supersaturation was sufficient to maintain continuous growth. Undercooling by more than 30° C always initiated spontaneous nucleation of many crystals. In the case of the normal alkali molybdate and tungstate compositions, BeO solubility was so low at all temperatures below 1400° C that no reasonable amount of undercooling initiated the onset of nucleation. However, as the moles of MoO₃ or WO₃ increased beyond 0.25

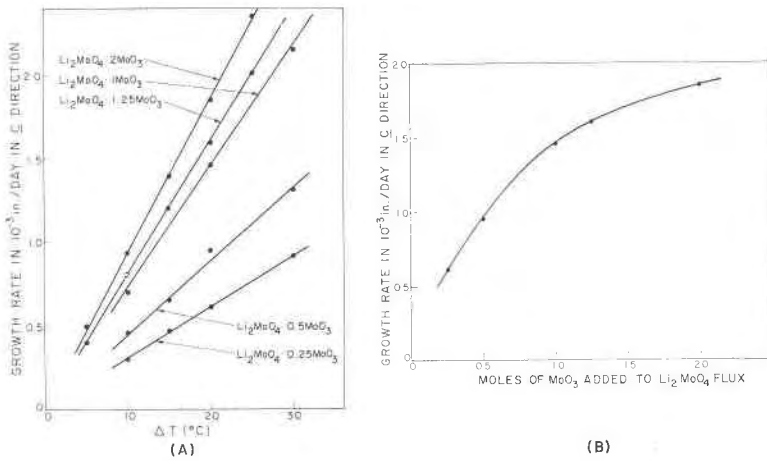


FIG. 4. Dependence of BeO growth rates using the modified Kruger-Fincke technique on (a) undercooling in a variety of Li_2MoO_4 - MoO_3 compositions at a nominal furnace temperature of 1100° C; and on (b) the composition of Li_2MoO_4 - MoO_3 fluxes at a nominal furnace temperature of 1100° C and a temperature gradient of 20° C.

m/o, supersaturation levels increased due to increased solubility, and growth rates increased in a manner illustrated in Fig. 4(b) for the case of lithium molybdate fluxes.

Another interesting phenomenon observed during the employment of the steady-state thermal gradient technique was the recognition of regions with differing nucleation thresholds. These nucleation regions have been observed at other laboratories (Austerman, 1963) in the case of lithium molybdate fluxes and appear to be a very general phenomenon present in all flux systems studied. In lithium dimolybdate, for example, nucleation did not occur below 1000° C, Region I; occurred only on BeO substrate material between 1000° C and 1250° C, Region II; and took place on both BeO substrates and platinum container above 1250° C, Region III. Transition temperatures for other compositions in this system were different but closely paralleled curves of constant solubility, Fig. 2(b). These data suggest that the transition temperatures define regions of critical supersaturation for nucleation and growth. Thus, for $\Delta T = 20^{\circ}$ C, nucleation does not occur at all in the Li_2MoO_4 system when the BeO solubility is less than 5 m/o, occurs only on BeO substrates when the solubility is 5–15 m/o, and on both BeO and platinum above 15 m/o. This hypothesis is consistent with estimates of transition temperatures in other systems which were shifted approximately in relation to the solubility of BeO in the flux composition and with the dependence of the

transition temperatures on the temperature differential employed: for example, as ΔT increases the temperature at which nucleation occurs on the platinum container decreases and vice versa. Perturbations of these nucleation regions by adding controlled amounts of impurities to the flux are discussed under "Impurities." It also seems likely that the critical regions of supersaturation are defined and maintained by interfacial energy relationships (Van Hook, 1961) in a manner not clearly understood at the present time. Region II is, of course, the most important area of the three regions, since it is within this field that single crystals can be most efficiently grown and enlarged.

The BeO crystals grown in alkali vanadate, molybdate, and tungstate fluxes show a very wide variation in habit, with the appearance of combination forms of four basic crystal habits, namely, prismatic, pyramidal, platy and dendritic. These basic crystal habits are shown in Fig. 5 (a-d). Similar habit variations have been reported for ZnO (Strunz and Meldau, 1950) and AlN (Kleber and Witzke, 1961). The prisms and pyramids normally grow in the negative polar direction, whereas plates generally are attached to substrates on edge and grow in a nonpolar direction (Austerman, *et al.* 1963; Smith *et al.* 1964). Two-circle optical goniometric measurements show that prisms are bounded by the first-order prism (10.0), the positive hemipyramid (10.1) and the negative pedion (00. $\bar{1}$). The minor forms corresponding to (00.1), and (10. $\bar{1}$), are also occasionally observed. These forms are in agreement with those reported for natural crystals (Aminoff, 1925). The pyramids and plates, which are in reality severely truncated pyramids, are bounded by the (10.1) pyramidal face, a large complex negative pedion (00. $\bar{1}$), and a smaller positive pedion face (00.1). Actually, the negative termination on most pyramidal and prismatic crystals is a complex surface composed of several forms. Usually the dominant form is a flat hemipyramid of the type $\{h0\bar{l}\}$ with $\bar{l} \gg h$. The faces are curved and definite integral values for h and l are not possible. Thus the surface is best considered to be composed of vicinal faces. Reentrant grooves are common along the edges of the pyramid composed of several alternations of adjacent faces. On many crystals another, sharper pyramid is present at the apex of the negative surface. The faces of this pyramid are also curved. This form, however, is the positive pyramid of a core of reversed polarity. This interesting type of polar twin is discussed in more detail under "Twinning." Another curved vicinal form which commonly appears is near $\{11.1\}$.

The optical properties of the crystals are uniaxial positive with indices of refraction $\omega = 1.719$ and $\epsilon = 1.733$.

Crevice flaws and fluid inclusions increased with increasing temperature or moles of oxide added to the normal flux composition, or both. These flaws usually contain frozen flux or other debris. They are usually

aligned to two principal crystallographic directions, (00.1) and (11.0), and in many cases appear to be associated with twin boundary regions.

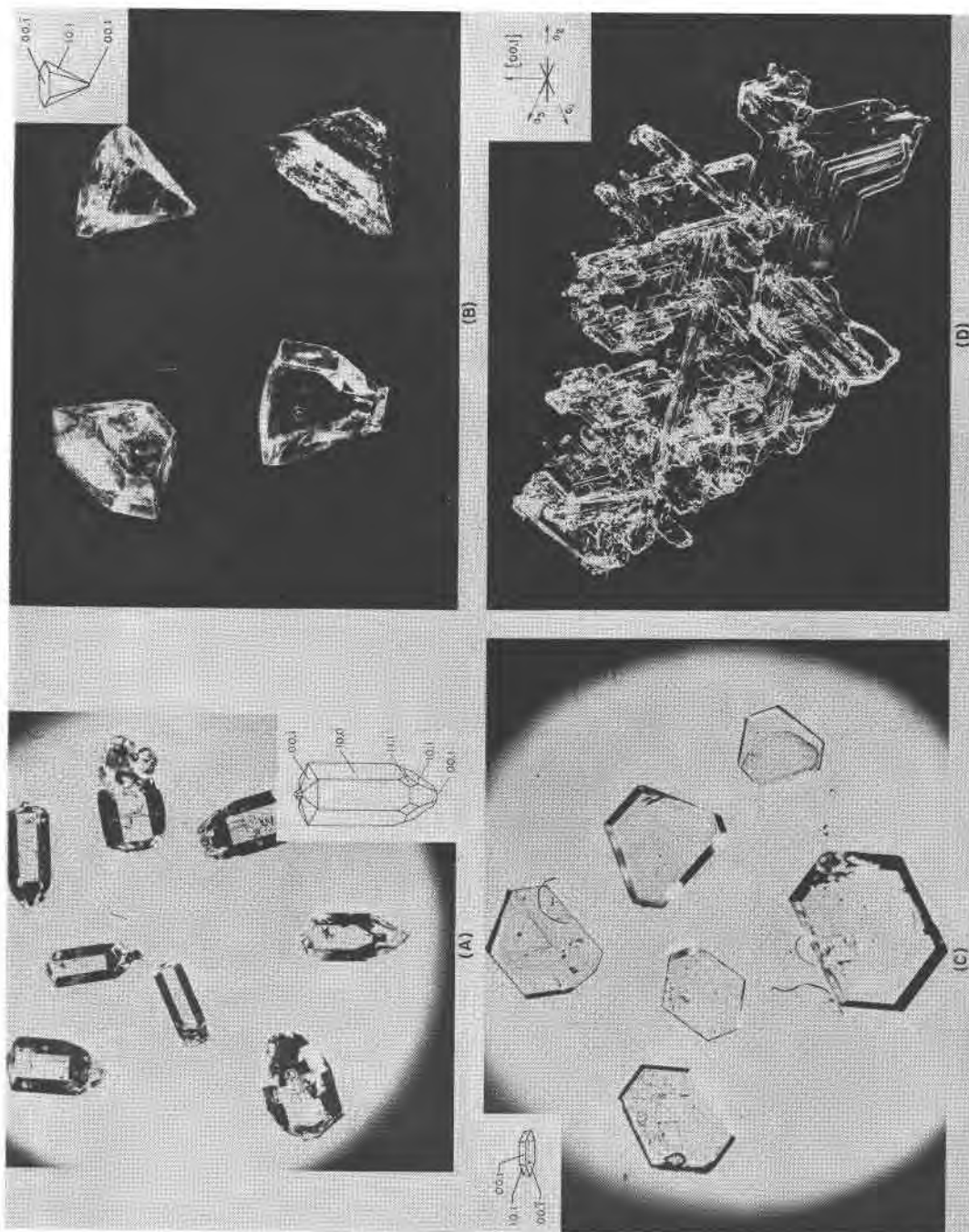
The appearance of the four basic crystal habits depends on the temperature and/or the supersaturation in the flux. These relationships are illustrated in Fig. 6 for the particular case of the system $\text{BeO-Li}_2\text{MoO}_4\text{-MoO}_3$. Essentially identical results were obtained in other molten alkali molybdates, tungstates, and vanadates, but the habit-transition temperatures and growth rates shifted approximately in conformity with differences in the melting point of the flux and BeO solubility. The effect of changing the temperature and supersaturation on the habit of a particular crystal was observed by immersing prismatic crystals in a flux composition and temperature where normally plates are grown. The continued growth of these transferred crystals assumed a platy habit.

Referring to Fig. 2a and previous discussions, it is clear from Fig. 6 that the important parameter, determining whether a BeO crystal will be either a plate (length/width < 0.81) or a prism (length/width > 0.81), is the temperature. Supersaturation has a smaller, non-systematic effect and is important in determining positions of nucleation zones and growth rates. Pyramids (length/width = 0.81) and dendritic forms are rare and occur under rather narrow conditions of temperature and/or supersaturation. Since the habit-transition temperatures are not sharp, overlapping occurs, and combination forms of all the basic crystal types appear. It is important to mention that these data apply (a) for temperature differences of 20° C, (b) for nucleation on non-oriented substrates, and (c) for systems not containing controlled amounts of impurities.

In slow cooling experiments, unlike the modified Krüger-Fincke method, the level of supersaturation of the solute varies with temperature and cooling rates. Consequently, the crystals experience a continuously changing growth environment and unique habit-temperature relationships are not observed. The amount of BeO precipitated is controlled by the initial and final temperatures, the volume of flux used, and the slope of the liquidus. In spite of these perturbations, crystals of BeO grown from PbO and PbO-PbF₂ mixtures were always well formed and were about the same size. This suggests that nucleation apparently occurred simultaneously over most of the substrate at optimum levels of supersaturation under the cooling rates employed, *i.e.*, (4° C/h).

These crystals grew in the positive polar direction and had essentially three different habits. In pure PbO, the habit was prismatic and rarely exceeded 0.125 in. in length. They are bounded by first-order prism planes (10.0) and on the other end by a hemipyramid modified sometimes by a small pedion (00.1).

As the concentration of PbF₂ in the PbO flux increases, the rate of growth in the (00.1) direction relative to the growth in the (11.0) direction



increases. Thus, in 25-m/o PbO-75-m/o PbF₂ mixture, the habit is acicular. The crystals are bounded by first-order prism planes and elongated in the *c* crystallographic direction. Many of these crystals are hollow prismatic columns and show hopper development on both basal and prism faces. In a 50-m/o PbO-50-m/o PbF₂ mixture, the growth is characterized by needles or "whiskers." The properties of these crystals were discussed in the preceding paper (Newkirk and Smith, 1964).

The impurities determined by emission spectrochemical analysis are commonly: lead, 100 ppm; boron, 10 ppm; iron, 50 ppm; and silicon, 20 ppm. The crystals are uniaxially positive with indices of refraction $\omega = 1.719$ and $\epsilon = 1.733$.

Hydrolysis of BeF₂ vapor. Crystals grown by hydrolyzing BeF₂ vapor are shown in Fig. 7. These crystals, which have grown to approximately 0.50 in. in length, appear to be of high quality, and are not twinned. These best ones contain no inclusions large enough to resolve by the optical microscope. The high growth rate, 0.125 in./day, results in a somewhat more complex morphology than in the other methods, but the habit is still dominantly prismatic. No other growth habit was observed. The crystals are uniaxial positive with refractive indices of $\epsilon = 1.730$ and $\omega = 1.715$, differing slightly from what is normally attributed to BeO. Typical emission spectrographic analysis showed the impurities and their concentrations to be Al, 60 ppm; Ca, 20 ppm; Fe, 100 ppm; Mg, 30 ppm; Si, 30 ppm; Ti, 40 ppm; and F, 1000 ppm. The similarity in ionic radii between oxygen and fluorine makes substitution in BeO structure relatively easy and undoubtedly accounts for the anomalous refractive indices of the crystals.

Hydrothermal environments. Crystals grown in hydrothermal environments had essentially the prismatic habit illustrated in Fig. 8. No other growth habit was observed. These crystals are 0.125 in. long and grew in the positive polar direction at rates approaching 0.005 in./day. The refractive indices were found to be similar to those obtained from the flux-grown crystals. The crystals appeared to be of the highest quality.



FIG. 5. A typical batch of BeO crystals grown in molten alkali vanadate, molybdate and tungstate fluxes using the modified Krüger-Fincke method. Four basic crystal habits appear, namely (a) prisms, (b) pyramids, (c) plates, and (d) dendrites. The prisms and pyramids normally grow in the negative polar direction, but the plates are generally attached to substrates on edge and grow in a non-polar direction. The crystals are approaching 0.250 inch in the longest dimension.

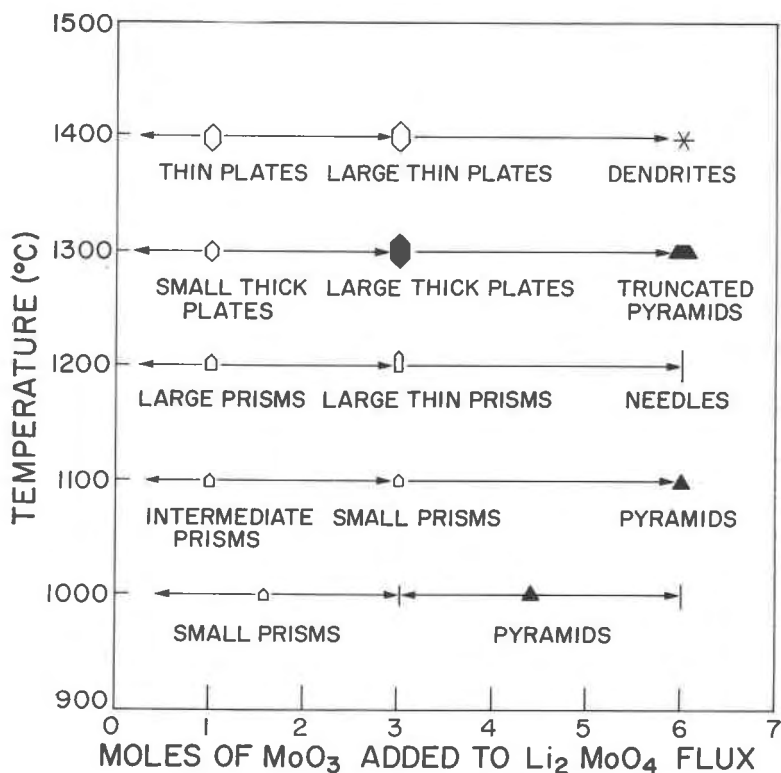


FIG. 6. Variation of BeO crystal habit with temperature and supersaturation in $\text{Li}_2\text{MoO}_4\text{-MoO}_3$ fluxes using the modified Krüger-Fincke method.

Emission spectrographic analysis showed the major impurities and their concentrations to be Si, 100 ppm; Fe, 10 ppm; and B, 7 ppm. Corrosion problems prevented long time runs from being conducted and the crystals shown are the largest grown by this technique. However these data demonstrate the potentialities of this technique for the growth of large, high-purity crystals and studies using this technique are continuing.

TWINNING

Twinning is a common growth feature and is observed in all environments. Twinning is not unique to BeO and is reported for many other wurtzite-like compounds. Dana's System of Mineralogy lists twins on (10.1), (10.2), (10.3), (11.1), and (11.2) for aluminum nitride (AlN) and the minerals wurtzite (ZnS), greenockite (CdS), zincite (ZnO), and bromellite (BeO). All the minerals show the polar twin (00.1).

Twinning in large crystals of BeO follow one twin law, with either

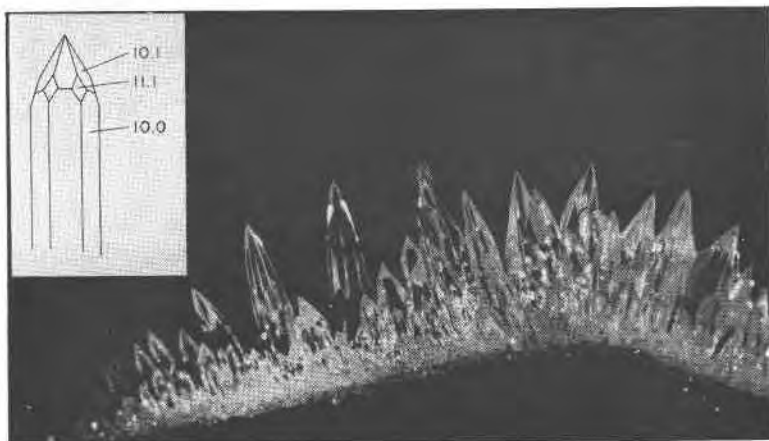


FIG. 7. A typical batch of BeO crystals grown by hydrolyzing BeF_2 vapor in air at 1000°C . The largest individual crystals are 0.5 in. long and grow at rates approaching 0.125 in./day. The habit is obvious: hexagonal prisms elongated along the c -crystallographic axis and growing in the positive polar direction. Note the complex facial development on the pyramidal surfaces. No other growth habit was observed in this environment.

(00.1) or $(00.\bar{1})$ as the twin plane. The (11.2) and (10.3) twins observed (Newkirk and Smith, 1964) among microcrystals of BeO and discussed in the previous paper were not noted in any of the many batches of crystals

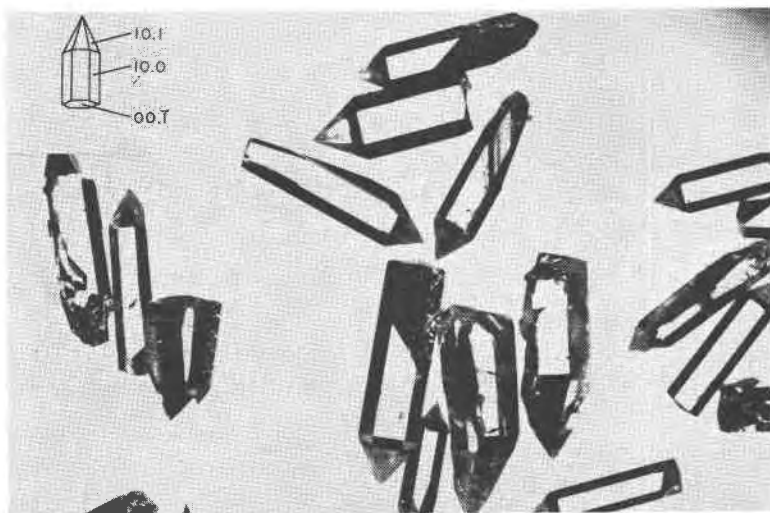


FIG. 8. A typical batch of BeO crystals grown in 2.03 M NaOH solutions at $400\text{--}420^\circ\text{C}$ and 2000 bars. The 0.125 in. long crystals have a prismatic habit and grew in the positive polar direction at rates approaching 0.005 in./day. No other growth habit was observed in this environment. The crystals are of the highest quality and purity and are not twinned.

examined in this study. The polar twin shows many different appearances. Figure 9(a) shows a contact twin with two reversals of polarity and Fig. 9(b) a typical penetration type twin. Some prismatic crystals have a core of reversed polarity along the length of the crystal as evidenced by a small pyramid on the otherwise blunt terminal end of the crystal, Fig.

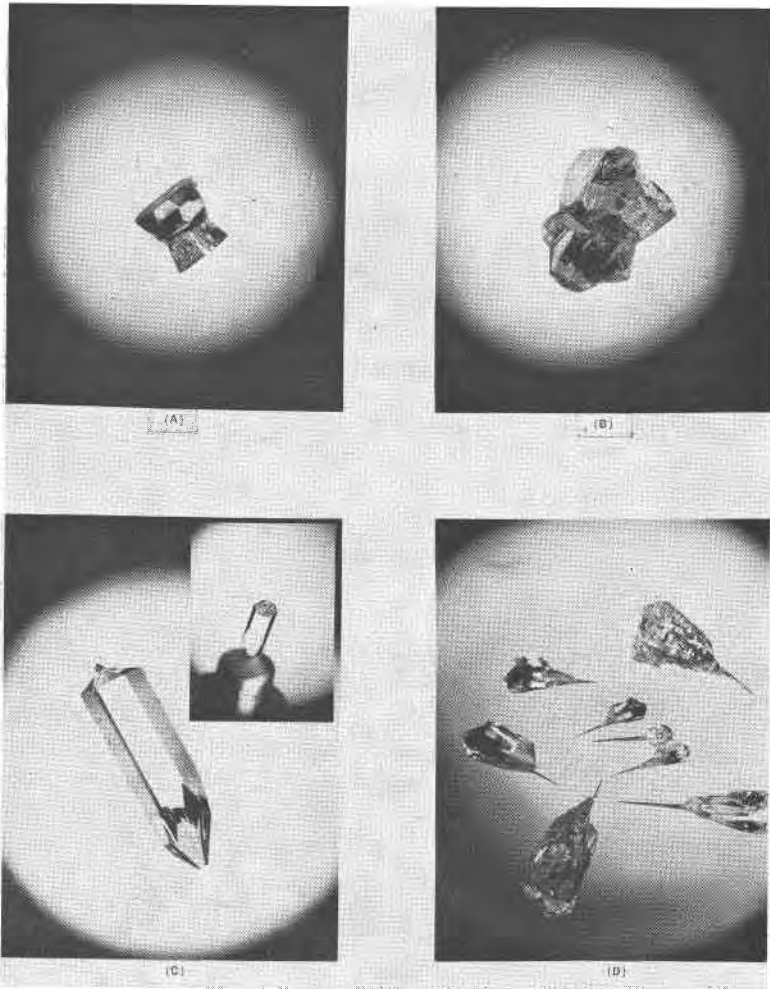


FIG. 9. Twinning of BeO macrocrystals follows one twin law with either the (00.1) or $(00.\bar{1})$ as the twin plane. Two types of twins are observed, contact or penetration. A typical contact twin with two reversals of polarity is shown in (a). The penetration twin can be either partial, as in (b), or complete, as in (c). The insert in (c) shows the complex development of the large negative pedion. (d) Crystals of BeO after etching for 7 hours in H_3PO_4 at $150^\circ C$. The small crystal which forms a core of the complete penetration twin is clearly revealed as a tail.

9(c). The core is easily observed in Fig. 9(d) which shows several crystals after being etched in phosphoric acid at 150° C. for 7 hours. Another example of this polar twin which has been reported by Austerman (1962) is found among crystals with a platy habit. This twin type, which has an irregular contact surface perpendicular to the basal plane, occurs only rarely in any of our crystals. To identify the polarity reversals, the polar morphology has proved most valuable. With the exception of the core twin, the morphology of the twin halves are usually in doubt.

Because the crystal structure of BeO is controlled by the hexagonal close packing of the oxygen atoms with the small beryllium atoms in the tetrahedral holes, the halves of the twin on opposite sides of the composition surface probably have a continuous oxygen structure. The only difference is the change of the beryllium atoms from one set of polar tetrahedral interstices to the other. Local charge balance may be retained without requiring vacancies; however, some surfaces may require vacancies.

Figure 10 shows a schematic illustration viewed perpendicular to the c axis of the composition planes (10.0) and (00.1). The (10.0) surface does not require any omissions in the structure, but does necessitate a distortion in the tetrahedral coordination configurations and results in close Be-Be distances. The (00.1) surface requires the omission of one half of the beryllium atoms on either side of the oxygen layer defining the composition plane. If the BeO structure is pictured as stacked double layers of equal numbers of triply-bonded beryllium and oxygen atoms, the layer at the composition plane is a triple layer. The omission of beryllium atoms in the layer will restore the local charge balance. The oxygen atoms in the layer, however, are no longer tetrahedrally coordinated but form only three bonds to beryllium neighbors.

Twinning with a composition plane of (00.1) results in a more complex boundary region. Assuming that the oxygen network is continuous across the composition plane, the stacking of double layers has a charge balance problem, because the beryllium atoms associated with the adjacent double layers are adjacent to each other. The resulting high repulsive energy would make the boundary unstable. Eliminating one-half of these beryllium atoms would create a local charge balance which would have to be compensated by the development of vacancies in nearby double layers or by an additional beryllium layer at the surface of the crystal. The vacancy concept seems more probable because the charge balance would be attained over a much smaller range within the crystal.

The details of the composition surfaces in actual twins have not been systematically studied, but the evidence already collected seems to indicate that the (00.1) and (10.0) composition planes are represented. However, crystals twinned on the (00.1) plane show very complex composition

surfaces. The lack of a good etchant for surfaces other than the basal planes prevents routine study of these twin boundaries. If the generalization indicated above is true, the frequency of appearance of twin types is in accordance with the ease of formation of a stable composition surface. In general, contact twins are found twinned on $(00.\bar{1})$, whereas twinning on (00.1) results in either a penetration twin or a core of opposite polarity. The effects of specific impurities on initiating twinning in the various environments is discussed under "Impurities."

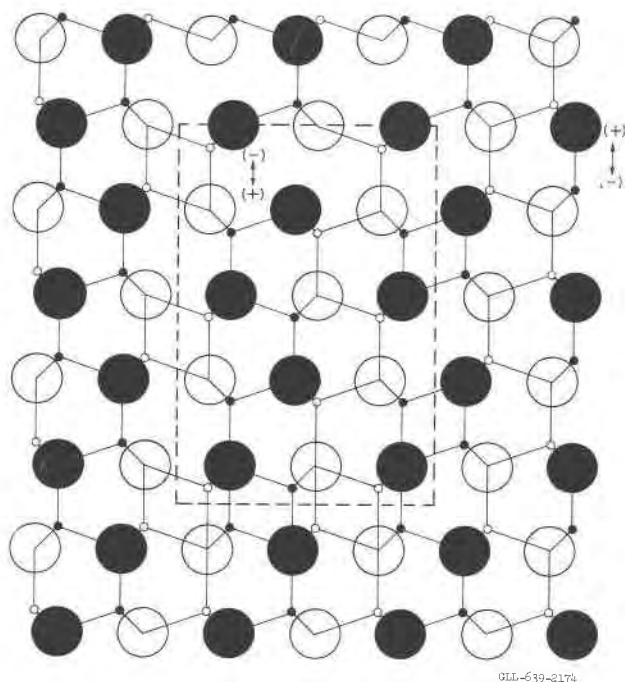


FIG. 10. Shows a schematic illustration of the proposed atomic configuration of the composition plane (10.0) and $(00.\bar{1})$. The small balls are beryllium and the large balls oxygen atoms. The unfilled balls are at $\frac{1}{2}$ elevation, the filled balls at 0 elevation. The (10.0) surface does not require any omissions in the structure, but does necessitate a distortion in the tetrahedral coordination configurations and results in close Be-Be distances. The $(00.\bar{1})$ surface requires the omission of one half of the beryllium atoms on either side of the oxygen layer defining the composition plane.

ENLARGEMENT OF CRYSTALS

The enlargement of polyhedral crystals was carried out by nucleation and subsequent long term growth on non-orientated polycrystal substrates using the Krüger-Fincke flux method. Enlargement of single crystal seeds by this technique is also being exploited and will be reported

at a later date. This technique was chosen because it was simpler and more reliable to operate over long periods of time than the other methods developed and crystals were desired which had a minimum of anion impurities or defects. The platinum containers used were either similar to those previously described, or vessels 6.0 in. in o. d. and 12.0 in. long. These large containers were filled only to one-half maximum capacity with 5 kg of flux. The only difference in the experimental arrangement between the two types of containers was that the larger vessels contained a perforated baffle (40% open area) and were rotated about the vertical axis in the furnace. The baffle, which rests 1.0 in. above the floor, serves two purposes: (1) it creates zones of uniform temperature by localizing the temperature differential at the baffle, and (2) during rotation, prevents polycrystalline substrates and single crystal seeds from floating into the hotter zone. Rotation of the flux continuously cleans growing crystal surfaces, minimizes concentration and temperature gradients, and in general improves overall crystal quality. Good quality crystals were grown using the following flux composition and temperature parameters:

Top temperature of container—1060° C

Bottom temperature of container—1030° C

Temperature differential—30° C

Composition of flux— $\text{Li}_2\text{MoO}_4 \cdot 1.25 \text{ MoO}_3 + 0.25 \text{ w/o Li}_3\text{PO}_4$.

These conditions were established on the basis of previous growth experience and on the physical chemistry of the various solvent systems. The purpose of the phosphate additive is to aid in promoting over-all high crystal quality as discussed under "Impurities." It should be mentioned at this point that this flux composition appears to be an excellent solvent, not only for BeO, but, for a wide variety of other oxide materials. In fact, using the Krüger-Fincke technique, large crystals have been grown of Al_2O_3 , ZrO_2 , TiO_2 , Be_2GeO_4 , Be_2SiO_4 , doped and undoped $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, ZrSiO_4 , and BeAl_2O_4 . The level of supersaturation under these conditions, calculated from the solubility of BeO and the slope of the liquidus curve at 1100° C., is about 1 m/o. Individual crystals, harvested after 3 months' time, weigh approximately 0.5 carat and approach 1 cm in length. The crystals are clear and colorless and have a dislocation density of 1/crystal. A typical emission spectrographic analysis showed the impurities and their concentrations to be: Li, 400 ppm; Mo, 500 ppm; B, 15 ppm; Fe, 55 ppm; and Si, 25 ppm. Optical and electron microscopic examination of sectioned crystals reveals the presence of two types of flaws. The first type is readily discernible at magnifications to 1500X and appears to be primary fluid inclusions, 5–250 μ in size. These inclusions undoubtedly contain occluded flux which would account for the high concentration of lithium and molybdenum in the crystals and density values which are always slightly higher than theoretical. Systematic

etching of thin sections, followed by examination of the surfaces at magnifications above $1500\times$, reveals the second type of flaw; namely, areas of reversed crystallographic polarity. A compilation of other pertinent crystal data is available on request (Newkirk and Smith, 1963A).

Measurement of growth rates normal to basal surfaces as a function of temperature indicate that the enlargement process has an activation energy of 15 kcal/mole. This value, when contrasted with 3 kcal/mole for diffusion in liquids indicates that the rate limiting step is not involved in the flux diffusion field; an observation which has important implications regarding the growth mechanism in these systems.

MECHANISMS OF GROWTH

Polyhedral and dendritic growth in molten salt solvents. It is generally believed that the growth of crystals from a solvent phase proceeds by the spreading of individual layers over the bounding surfaces. Layers on less densely packed surfaces move at faster rates than on more densely packed surfaces and hence high index faces are quickly eliminated. The active sites for growth are recognized as kinks in the steps that bound the individual growth layers. The twinning phenomenon observed, the consistent pattern of habit change with temperature, and the large activation energies required for growth in molten fluxes are consistent with the view that volume diffusion is not the rate controlling step in the growth process.

Of particular interest is the elucidation of the mechanism which controls the pattern of habit change with temperature in molten fluxes. The questions that arise are (1) what path is taken by the solute molecules from the solvent phase to a kink site, (2) what controls the rate of advance of the growth layers, and (3) what is the source of these layers? Let us consider the first two questions in this section and discuss the last question later. Two paths might be possible, depending upon the relative importance of surface diffusion and nucleation mechanisms in the growth process. In either case, the important rate controlling parameters must be both face dependent and sensitive to temperature changes. Where surface diffusion mechanisms are important as in the growth of crystals from the vapor phase, the rate controlling parameter has been discovered; its importance in the growth of crystals from a solvent phase, however, has yet to be demonstrated. In contrast, nucleation mechanisms have not been so clearly defined. The important parameter involved in the surface diffusion mechanism is the mean free path for diffusion, X_s , defined as the average distance which a molecule travels on a crystal surface before evaporating (Burton *et al.* 1951). Values of X_s commonly lie between 10^{-6} to 10^{-3} cm (Calrera and Coleman, 1963). More important, however, is the fact that X_s is face dependent and varies in a transcendental-exponential

manner with temperature as Mason has experimentally shown recently for the growth of ice crystals (Mason *et al.* 1963). The assumption that X_s varies with temperature on BeO surfaces in a manner similar to that on ice crystal surfaces offers an immediate explanation for the twinning phenomenon observed and the variation of BeO crystal habit with temperature, namely: large thin plates \rightarrow severely truncated pyramids \rightarrow long thin prisms \rightarrow pyramids, as the temperature changes from 1400 to 1000° C. Surface diffusion would be different on each of the four equilibrium faces, *i.e.*, the positive and negative pedions, X_s^{e+} and X_s^{e-} respectively, pyramidal X_s^p and prism faces X_s^m . The curves would intersect at three points, giving four temperature ranges in which the ratio $(X_s^{e+} + X_s^{e-}) / (X_s^p + X_s^m)$, $X_s^p / (X_s^m + X_s^{e+} + X_s^{e-})$, and $X_s^m / (X_s^p + X_s^{e+} + X_s^{e-})$ alternate between being larger than, or smaller than, 0.81. When $(X_s^{e+} + X_s^{e-}) / (X_s^p + X_s^m) < 0.81$, the crystals will be essentially plate-like. Whether the plates have prism faces depends on $X_s^m > 0$; and whether the plates are thick or thin, depends on relationships between X_s^{e+} and X_s^p . Prisms will develop at temperatures for which $X_s^m / (X_s^p + X_s^{e+} + X_s^{e-}) > 1.63$. In a similar manner, pyramids develop at temperatures for $X_s^m = 0$ and $X_s^p / (X_s^{e+} + X_s^{e-}) = 0.81$. In the last two cases, the growth direction is determined by whatever basal surface is energetically the most stable under the environmental conditions employed.

The crystals will continue to grow as polyhedra as long as excess material is efficiently redistributed over the surface by diffusion. However, as the supersaturation of the environment increases, surface diffusion becomes unable to cope with the nonuniform deposition, so the corners and edges grow to form hopper crystals, dendrites and other skeletal forms. The mechanism under these conditions is analogous to the flow of rivers or the traffic flow on a Los Angeles freeway and is characterized by "bunching" processes (Lighthill and Witham, 1955). The limiting step is the rate of flow of growth layers to and from agglomerated regions. Comparison of photographs showing the surface structure of ice and BeO reveal similar terraced growth features 500–2000 Å in height marking the location of critical regions. It is important to remember the X_s^p is the only parameter that can never be equal to zero in this system because of the lack of a center of symmetry in the BeO crystal structure.

There will be an X_s dependence on temperature for each of the infinite number of possible faces in the wurtzite structure, and under nonequilibrium conditions these diagrams can undoubtedly be very complex. However, calculations of nucleation rates based on observed supersaturation levels and growth rates indicate that a nucleation mechanism might also be important during growth. For example, a calculation of the rate based on a supersaturation ratio of 1.04 at 1100° C. indicates that about 2×10^{19} nuclei/cm²/sec are potentially available for two-dimensional

nucleation. This number is orders of magnitude greater than the nucleation rate needed to allow for observed growth rates. Hence, it is quite clear that nucleation on BeO surfaces is being inhibited in some manner. In fact, at such high rates nucleation would probably occur directly at kink sites with very little surface diffusion taking place. The rate determining step in this process would then be involved in the decomposition of the solute-bearing species and in the ensuing adsorption process.

Undoubtedly, condensation coefficients would be different for the various equilibrium faces and would exhibit characteristic temperature coefficients. The rate of linear advance of a particular face would then be determined by its condensation coefficient; the largest faces occurring adjacent to the fastest growing faces. Selective adsorption of impurities and consequent changes in condensation coefficients could account for the different facial development observed. Rideal and Wiggins (1952) measured the evaporation pressure of different faces on sulfur crystals grown from organic solvents. By calculating condensation coefficients from these data they were able to account for the unique habit-temperature relationships observed during growth.

It is quite possible that both mechanisms are important in the growth of BeO crystals from the flux; *i.e.*, surface diffusion mechanisms are rate controlling at low supersaturation levels and nucleation mechanisms on surfaces are rate controlling at high supersaturation levels. Data obtained from measurements of surface diffusion on BeO, growth and evaporation kinetic studies, and effects of different substrate materials and electric fields on nucleation phenomenon, should improve our understanding of the mechanisms involved in the growth of BeO crystals.

Twinning. Three possibilities suggest themselves when attempting to rationalize the twin growth mechanisms, *i.e.*, either twinning occurred during the nucleation, or it occurred during subsequent crystal growth, or the substrate grain in the seed plate was itself twinned. Optical examination of polished and etched thin sections sampled from representative polycrystalline BeO seed plates reveals the presence of twinned grains, which is evidence for the last possibility. It is interesting, however, that the presence of 0.1 w/o MgO in the BeO substrates increases in the population density of the twinned grains, which closely parallels increases in the population density of twinned single crystals growing on magnesia-doped BeO substrates. Direct evidence for twinned vs untwinned nuclei has not been obtained. However, the fact that (1) not all BeO crystals growing in the negative polar direction are twinned, (2) twinned crystals grow also on platinum substrates, and (3) twinning can be catalyzed by selective impurities is evidence supporting the twinned nucleus hypothe-

sis. At first thought, this might imply a violation of basic concepts, since classical nucleation theory (Volmer and Weber, 1925; Becker and Döring, 1935; Gibbs, 1948) has always considered the particles to be homogeneous. However, Turnbull (1956) has pointed out the limitations in the classical nucleation theory, and recently Cahn and Hilliard (1958, 1959) have developed a satisfactory analysis of nucleation concepts based on a thermodynamic treatment of nonuniform systems. In their terminology, the nucleation of BeO polar twins is to be considered as nonclassical nucleation; an event which occurs at high supersaturations. Recently, Sears (1961) has discussed the conditions under which nonclassical nucleation of crystalline solids should be expected and has shown (Sears *et al.* 1963) that ZnO fourlings almost certainly nucleate as fourfold twins in a single homogeneous event. Fullman's (1957) analysis of the equilibrium form of crystalline bodies suggests a second alternative: the BeO polar twin might be more stable than a single crystal in its equilibrium form because of electrical charge problems arising from spontaneous polarization. These two possibilities can be distinguished when a knowledge of the degree of supersaturation at the time of nucleation is obtained, since Fullman's model requires a low supersaturation.

If twinning occurred only during subsequent enlargement of the crystal, then impurity effects creating strains in growing surface layers, supersaturation changes and local non-isothermal conditions, or combinations of these phenomena might be suspected. It is important to note that in the mechanism proposed for the growth of polyhedral BeO crystals from molten salt solvents, the X_s versus temperature curves for the two basal surfaces would not be identical and thus reflects differences either in specific surface free energy or in condensation coefficients. Clearly, any effect(s) which reverse(s) the normal relationship will reverse the growth direction.

However, regardless of the initial growth mechanism the six re-entrant corners on the complex negative basal pedion would be expected to be favored sites for the deposition of material because of the high level of supersaturation existing within this area. These re-entrant corners must, at least initially, be perpetuated. However, the re-entrant corners would fill in and cease to an important area for nucleation and growth. The fact that these areas do not fill in and that the surrounding crystal continues to grow in the negative c -direction, indicates that the central core crystal is advancing simultaneously in the positive c -direction, probably by another mechanism. As we shall see later, the key to this mechanism is the presence of dislocations in the central core with $[00.1]^*$ Burgers vectors. This behavior is to be contrasted with the growth of paraffin dendrites (Dawson, 1952), in which the corner cannot grow out, and

germanium dendrites (Hamilton and Seidensticker, 1960), and dendrites of other III-V compounds (Willardson and Goering, 1962), in which a minimum of two twin planes are a necessity for continued rapid growth. As already mentioned in the previous paper the twin plane mechanism is important in the growth of some of the microcrystals of BeO, and may also account for the growth of SiC, baddeleyite (ZrO_2), and many other natural minerals.

EFFECT OF IMPURITIES

Certainly, if surface diffusion of BeO molecules and/or a nucleation mechanism is important in controlling the growth of BeO crystals, then it should be possible to influence the generation and flow of individual layers by adding controlled amounts of impurities to the environment. In general, this is exactly what is observed. We have found that the addition to molten salt solvents of up to 0.5 w/o of cations and anions with ionic radii larger than 0.38 Å (for example, PbO, SnO₂, MnO₂, Al₂O₃, CaO, MgO, TiO₂, ZrO₂, LiF, Li₂SO₄) improves crystal quality but does not drastically alter growth rates or change habit, etc. Conversely, tetrahedrally coordinating cations with ionic radii less than 0.38 Å (i.e., B, Si, and P) change growth habits, increase growth rates, reverse normal polar growth direction, modify nucleation zones, and, in general, improve crystal quality. Phosphorous in particular appears to be a necessary ingredient in obtaining high quality crystals and flux compositions generally contain Li₃PO₄. Interestingly, Li₂Mo₂O₇ compositions at >1200° C. and containing >1.0 w/o Li₃PO₄ yield crystals having a complex morphology but with a predominantly platy habit. The majority of these crystals are free of twins. Thus it is now possible by adding controlled amounts of either boron or phosphorus to lithium molybdate fluxes to systematically vary both growth direction, twinning, and crystal habit. Efforts to exploit these phenomenon are in progress and findings will be correlated with habit control mechanisms operative in natural environments. In the case of silicon, additions of more than 0.1 w/o causes the preferential formation of phenacite.

The fact that boron produces a habit modification to crystals grown in molten fluxes, whereas phosphorous does not, suggests that boron is adsorbed on the surface and is incorporated into the crystal lattice. Conversely, phosphorous is not incorporated and is involved only in the nucleation step of the growth mechanism. Since boron (radius=0.20 Å) will readily fit into a tetrahedral site it seems likely that this impurity acts as a poison by adsorbing at growth steps, or kinks in growth steps in a manner described by Gilman *et al.* (1958). Possibly phosphorous is incorporated in a charged or neutral inorganic complex, such as phospho-

molybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_4 \cdot 9 \text{H}_2\text{O}$). One can speculate that the presence of phosphorous decreases the available number of BeO containing solvent species thereby reducing the level of supersaturation and correspondingly the growth rates. The over-all result is a more highly perfect crystal.

The addition of lithium fluoride vapor to BeF_2 vapor reverses the normal growth direction and causes extensive twinning to occur. This result adds support to the theory that impurities are important controlling factors in initiating twinning of beryllium oxide macrocrystals. In general, however, most impurities are ineffective and are rejected by the lattice, which is consistent with the nature of the close-packed BeO structure and in the case of molten molybdates and tungstates with the ability of these fluxes to complex interfering cations.

DISLOCATION SUBSTRUCTURE

Up until this section, we have considered only the kinematics involved in spreading of individual layers over the bounding crystal surfaces, and the question now arises as to the source of these layers on polyhedral and dendritic crystals. The fact that BeO crystals grow at a very low supersaturation ($< 2.0\%$) leads to the conclusion that sites are always present which make the two-dimensional nucleation process of new layers unnecessary. It was shown previously that when a single crystal was transferred into a new environment, the continued growth assumed a new habit characteristic of the new condition. Crystals growing on a BeO substrate in molten fluxes react differently, however, depending on the orientation of the substrate. For example, consider the habit of crystals growing on a tubular polycrystalline BeO substrate which has 95% of its grains orientated parallel to the "c" crystallographic axis and the long dimension of the tube. Crystals growing on the ends have a prismatic habit, but crystals growing on the sides of the tube are tubular or platy and attached at the vertex. Conversely, crystals growing on non-oriented tubes have only a prismatic habit, as would be expected from the temperature and supersaturation conditions employed in these studies. We interpret these results as being caused by the presence or absence of suitable sites for growth in the required vectorial directions. Overgrowth experiments on single crystal substrates indicate that nucleation occurs at impurities located at the surface of the crystal and that growth proceeds along the preferential directions $[00.1]^*$ and $[11.0]^*$.

Furthermore, in the case of the penetration-type twinned crystal, x-ray diffraction topographic analysis, Fig. 11(a) shows that the central core contains a screw dislocation with $[00.1]^*$ Burgers vector. The corresponding etch figures Fig. 11(b) reveal the location of impurities as they are exposed on the positive basal surface. Except for damaged surface

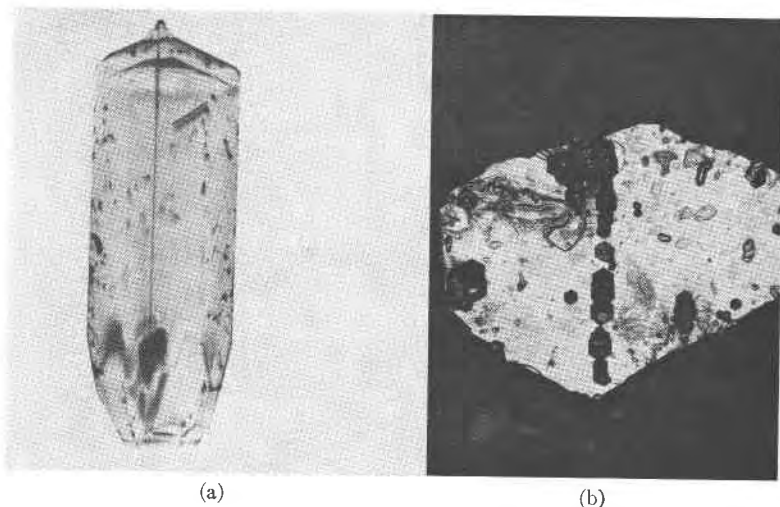


Fig. 11. (a) An (002) x -ray diffraction topograph of the BeO penetration twin (Fig. 9c) using the Lang technique. The central core of the twin contains a screw dislocation network with $[00.1]^*$ Burgers vector. (b) The hexagonal etch figures reveal the location of impurities they terminate on the (00.1) plane of the central core crystal.

layers, the substructure of the crystals is remarkably perfect. Thus, BeO should be an excellent environment for studying the generation and motion of induced dislocations.

As discussed before the presence of the $[00.1]^*$ dislocation network in the central core has important implications as regards the mechanism of growth. There seems to be little doubt that this type of crystal grows by the simultaneous advance of the central core in the positive c -direction through operation of screw dislocations and of the outer crystal in the negative c direction as material is added to the six re-entrant corners on the complex basal pedion. This mechanism employing the simultaneous operation of two classical mechanisms of crystal growth, appears to be unique to BeO. Studies of the BeO substructure are continuing and more-detailed results will be published at a later date.

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In a program of this magnitude, a great many people contributed their time and talents to make it a success. We would like to take this opportunity to acknowledge important contributions. D. R. Kingman helped perform most of the growth experiments described in this report. J. S. Kahn determined the optical properties of the crystals. The design for the vertical loading, rotating crystal furnace was conceived in the office of

J. P. Remeika and is modeled after several similar furnaces in operation at the Bell Telephone Laboratories. We wish to acknowledge the discussions we have had, both oral and written, with J. J. Gilman, University of Illinois; N. Cabrera, University of Virginia; R. Parker, National Bureau of Standards; S. B. Austerman, Atomics International; J. W. Cahn, General Electric Company; V. D. Frechette, Alfred University; A. Pabst, University of California; A. Higashi, Hokkaido University; R. H. Borg, Lawrence Radiation Laboratory; J. W. Kelly, Lucas Heights, Australia; B. J. Mason, Imperial College, London; and W. Clark, Oak Ridge National Laboratory, and N. A. Houlding of LRL on nucleation theory, crystal growth and twinning of oxide materials. The encouraging advice of C. F. Cline during the course of this work was always helpful.

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