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Crystallization of BeO, Be_2SiO_4, and SiO_2 From Li_2MoO_4–MoO_3

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Single crystals of phenacite (Be_2SiO_4), bromellite (BeO), and tridymite (SiO_2) were grown from a MoO_3-Li_2MoO_4 flux. Phenacite, with rhombohedral symmetry, grew in three distinct shapes with aspect ratios (length/width) as follows: needles (> 3), rods (> 1.1 to 1.5), and rhombohedral-faced crystals (≈ 1). The latter grew as single crystals; the others were twinned on the $(10\bar{1}0)$. For most experiments the temperature was held constant at 1165°C and the Li_2MoO_4/MoO_3 ratio at 1/16. The growth mechanism for crystallization was the evaporation of MoO_3. The system produced one to three phases depending on the BeO/SiO_2 ratio. Bromellite grew until a BeO/SiO_2 ratio of 0.8 was attained. It grew as a hemipyramidal crystal, that had a short prism with a curved $(000\bar{1})$ top or as a hexagonal plate. The pyramid- and prism-shaped crystals were twinned, although a few hexagonal plates were single. Tridymite grew in small hexagonal plates when the BeO/SiO_2 ratio was less than 1.5. The effect of temperature, nucleation, and flux composition on crystal shape, twinning, and occurrence is discussed.

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FOREWORD

This report is published by The Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04701-71-C-0172.

This report, which documents research carried out from June 1971 through September 1971, was submitted 6 March 1971 to Lieutenant William E. Belote, SYAE, for review and approval.

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Approved

A. H. Silver, Director
Electronics Research Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

William E. Belote
1st Lt., U. S. Air Force
Project Officer

ABSTRACT

Single crystals of phenacite (Be_2SiO_4), bromellite (BeO), and tridymite (SiO_2) were grown from a MoO_3-Li_2MoO_4 flux. Phenacite, with rhombohedral symmetry, grew in three distinct shapes with aspect ratios (length/width) as follows: needles (> 3), rods (> 1.1 to 1.5), and rhombohedral-faced crystals (= 1). The latter grew as single crystals; the others were twinned on the $(10\bar{1}0)$. For most experiments the temperature was held constant at 1165°C and the Li_2MoO_4/MoO_3 ratio at 1/16. The growth mechanism for crystallization was the evaporation of MoO_3. The system produced one to three phases depending on the BeO/SiO_2 ratio. Bromellite grew until a BeO/SiO_2 ratio of 0.8 was attained. It grew as a hemipyramidal crystal that had a short prism with a curved $(000\bar{1})$ top or as a hexagonal plate. The pyramid- and prism-shaped crystals were twinned, although a few hexagonal plates were single. Tridymite grew in small hexagonal plates when the BeO/SiO_2 ratio was less than 1.5. The effect of temperature, nucleation, and flux composition on crystal shape, twinning, and occurrence is discussed.

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I. INTRODUCTION

Bromellite (BeO) and phenacite (Be_2SiO_4) are difficult crystals to prepare because of the high toxicity of BeO. However, the demand for optically clear crystals justifies the extra precautions necessary. Bromellite is being used extensively as a high-temperature refractory, a dielectric, and as a moderator in gas-cooled nuclear reactors. Phenacite can be used in optical experiments where high optical quality, uniaxial, optically positive, centrosymmetric crystals are required.

The growth of bromellite and phenacite single crystals has been reported by Newkirk and Smith[1] and by Austerman.[2-5] The work of Newkirk and Smith dealt primarily with growth conditions, mechanisms, and habit changes. The work of Austerman was concerned with crystal growth, twinning, habit, and impurity effects. On the other hand, little work has been done on the growth of synthetic phenacite. Ballman and Laudise[6] have reported on its solubility in alkali molybdates and alkali vanadates, and it has been mentioned as a secondary phase in discussions of the growth of emerald.[7,8]

In this paper, the crystallization of BeO, Be_2SiO_4, and SiO_2 (a by-product) from a Li_2O-MoO_3 flux is characterized and discussed. Major emphasis is placed on phenacite and its habit changes. Although other work has indicated that this habit change is dependent on temperature,[6] we show that it is also dependent on the composition of the solute and flux.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The materials used in these experiments included high-purity grade BeO (Beryllium Technology Corp., Newbury Park, Calif.), high-purity grade ground quartz (Englehard Industries, Inc., Amersil Quartz Div., Hillside, New Jersey), high-purity grade Li_2MiO_4 (Chemical Procurement Laboratories, Inc., College Point, New York), and analytical reagent grade MoO_3 (Baker and Adamson Div., Allied Chemical Corp., Morristown, New Jersey). Standard-form 50-ml platinum crucibles were loaded with mechanically mixed powders of a predetermined composition and placed in a 800°C, preheated, SiC heating element box-type furnace with their lids tightly crimped. This furnace consisted of six evenly spaced (1 in. apart) elements placed horizontally 1 in. from its top. Insulation was provided by an inner and outer layer of fire bricks capable of sustaining 1650° and 1230°C, respectively. The area of the hearth was 9 in. long × 9 in. wide × 8 in. high. Power and control was maintained through the use of a SCR power supply and a pyrometric Pt/Pt 13 % Rh temperature controller. Although the furnace had a large vertical temperature gradient (150°C hotter at its top), the crucibles did not have a gradient because of the high thermal conductivity of the melt and crucible. Separate thermocouples were placed on the top and bottom of the crucibles during the experiments in order to obtain a measurement of temperature differences, if present. The furnace and BeO were handled in a controlled toxic area.[9]

Nearly all the experiments were conducted at a fixed growth temperature of 1165°C in order to show the dependence of the habit on solute composition. A few runs were grown at temperatures between 1180° and 1200°C and a few with increased amounts of Li_2C (Li_2MoO_4-3.5 MoO_3). Most of the runs were continued for five days. However, some were continued for three days in order to check the phases present. After allowing the furnace to fast cool to 900°C (1165° to 900°C in 1 hr), the crucibles were removed

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and allowed to fast cool to room temperature. No appreciable difference in weight loss, crystal yields, or characteristics was observed when the growth time was reduced from five to three days. The driving force for crystallization was the flux evaporation. The flux loss was probably due to the high vapor pressure of MoO_3. Weight loss was 68 to 79 wt% of the initial MoO_3 when a flux composition ration of 1/16 (Li_2MoO_4/MoO_3) was used and the temperature held constant at 1165°C. It was calculated that the final flux composition had a ratio of 1/2 to 1/3.25 (Li_2MoO_4/MoO_3). The addition of Li_2MoO_4 as well as SiO_2 lowered the weight loss. Compositions used in most of the experiments were: 15 mole % solute (BeO and SiO_2), 5 mole % Li_2MoO_4, and 80 mole % MoO_3. Crystals were removed from the solidified melt by first leaching in hot 30 % NH_4OH for 2 hr, then soaking in hot 25 % HCl for 2 hr or until all the flux was dissolved. Yields ranged from 47.5 % for a BeO/SiO_2 ratio of 1, which produced all three phases, to 70 % for a BeO/SiO_2 ratio of 0.1, which produced only tridymite. The size of the crystals ranged from 1 to 5 mm for BeO (Fig. 1), 1 to 7 mm for Be_2SiO_4 (Fig. 2), and as small as 10 to 100 μm, growing in clusters, for SiO_2 (Fig. 3).

A. PHENACITE

This is a centrosymmetric crystal that belongs to the trigonal-rhombohedral class $R\bar{3}$, which is characterized by the absence of all planes of symmetry and a trigonally symmetric vertical axis.[10] The crystal has a very open structure with a large unit cell (a_o = 12.75 Å, C_o = 8.41 Å). It is optically positive, has a Mohl hardness of 7.5 to 8 and a density of 2.97 to 3, is transparent in the visible, has a refractive index of ω = 1.6540 and ϵ = 1.6697, and has cleavage on the $(11\bar{2}0)$ face and twinning on the $(10\bar{1}0)$ face.

Three distinctly different shapes with aspect ratios (length/width) as follows were often observed in the same crucible (Fig. 2): prismatic needles (> 3), primatic rods (> 1.1 to 1.5), and rhombohedral-faced crystals (= 1). Although only a few of the prismatic equidimensional crystals were

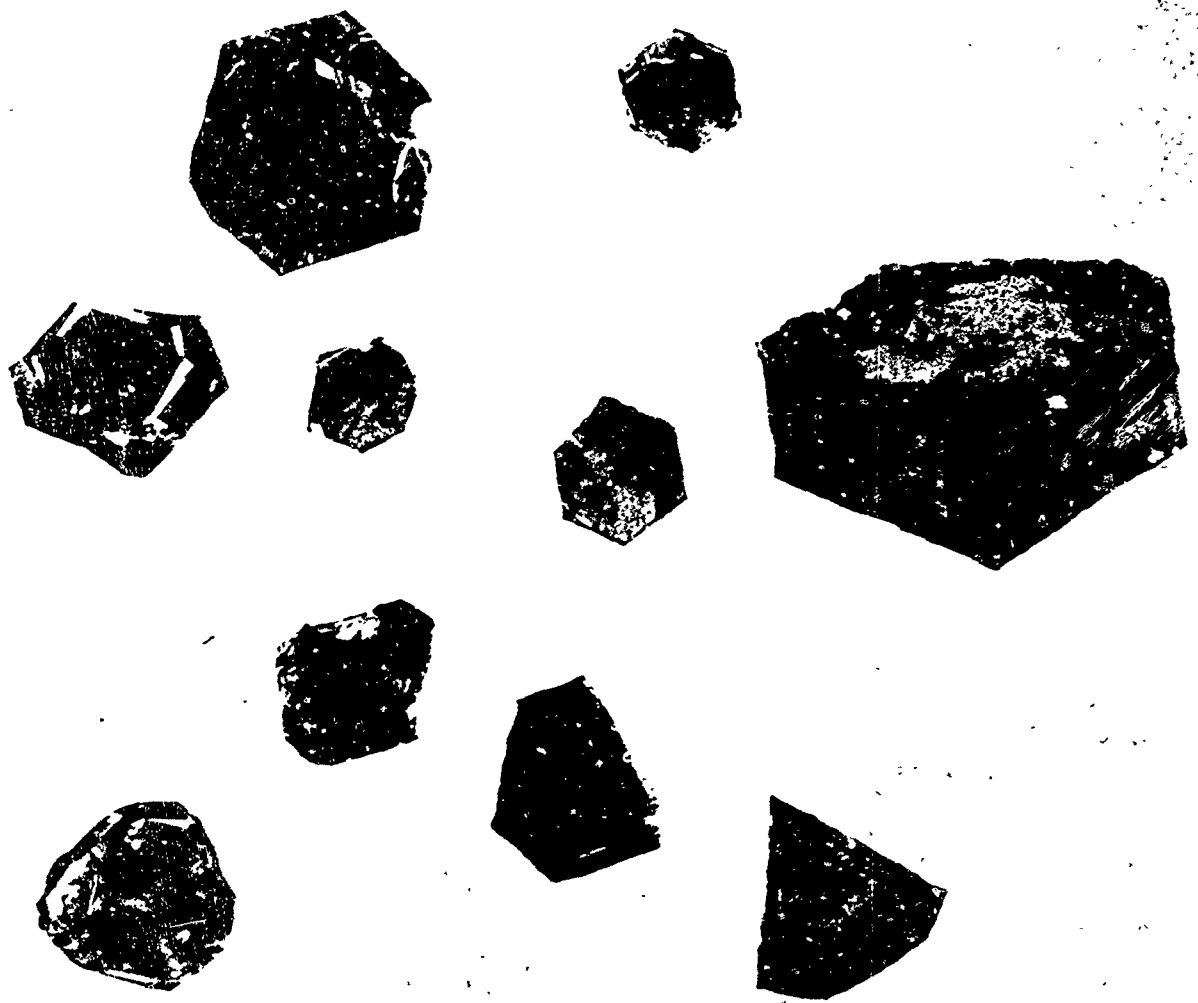

Figure 1. Bromellite Crystals (1 to 5 μm)

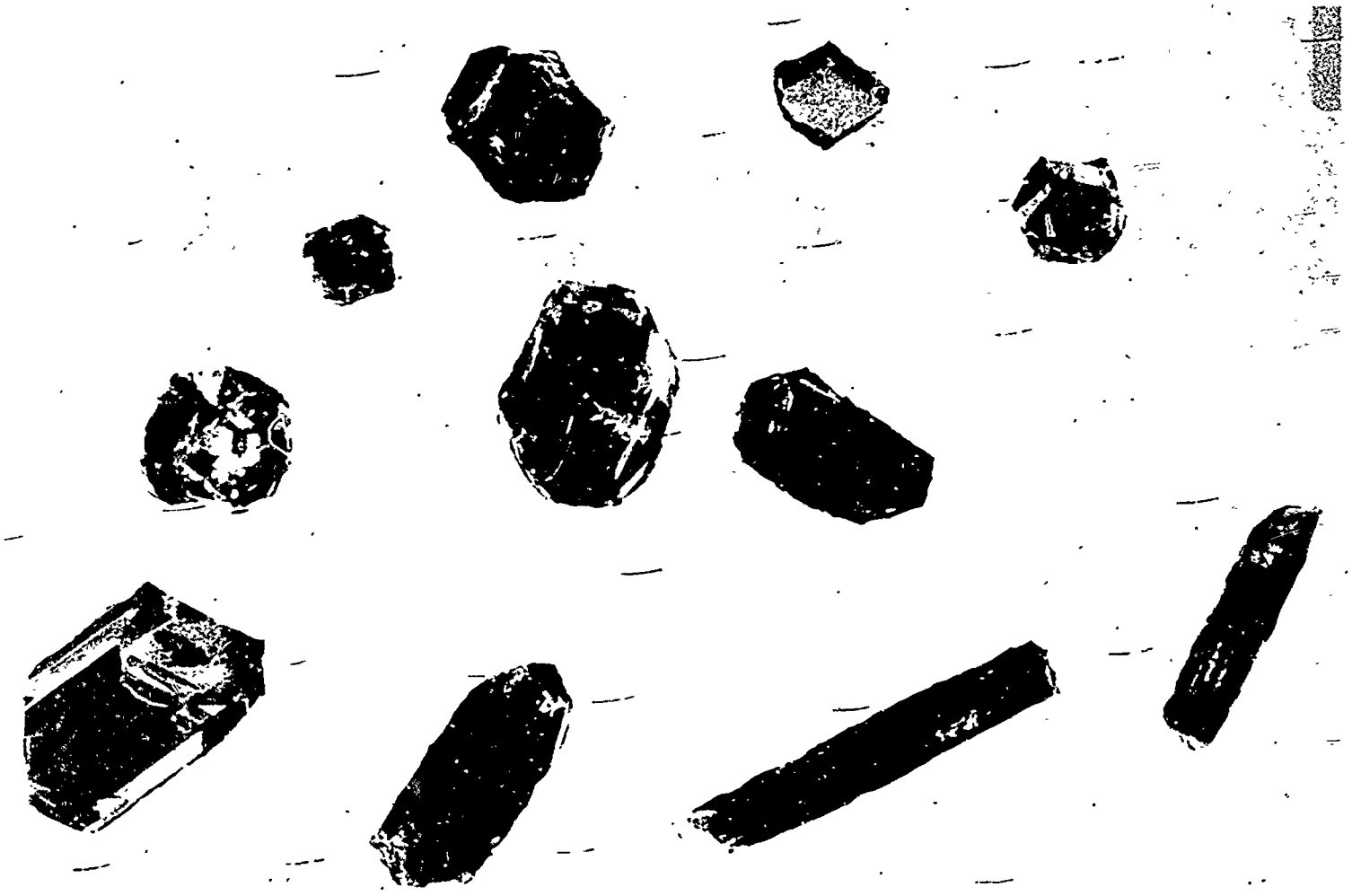

Figure 2. Phenacite Crystals (1 to 7μm)

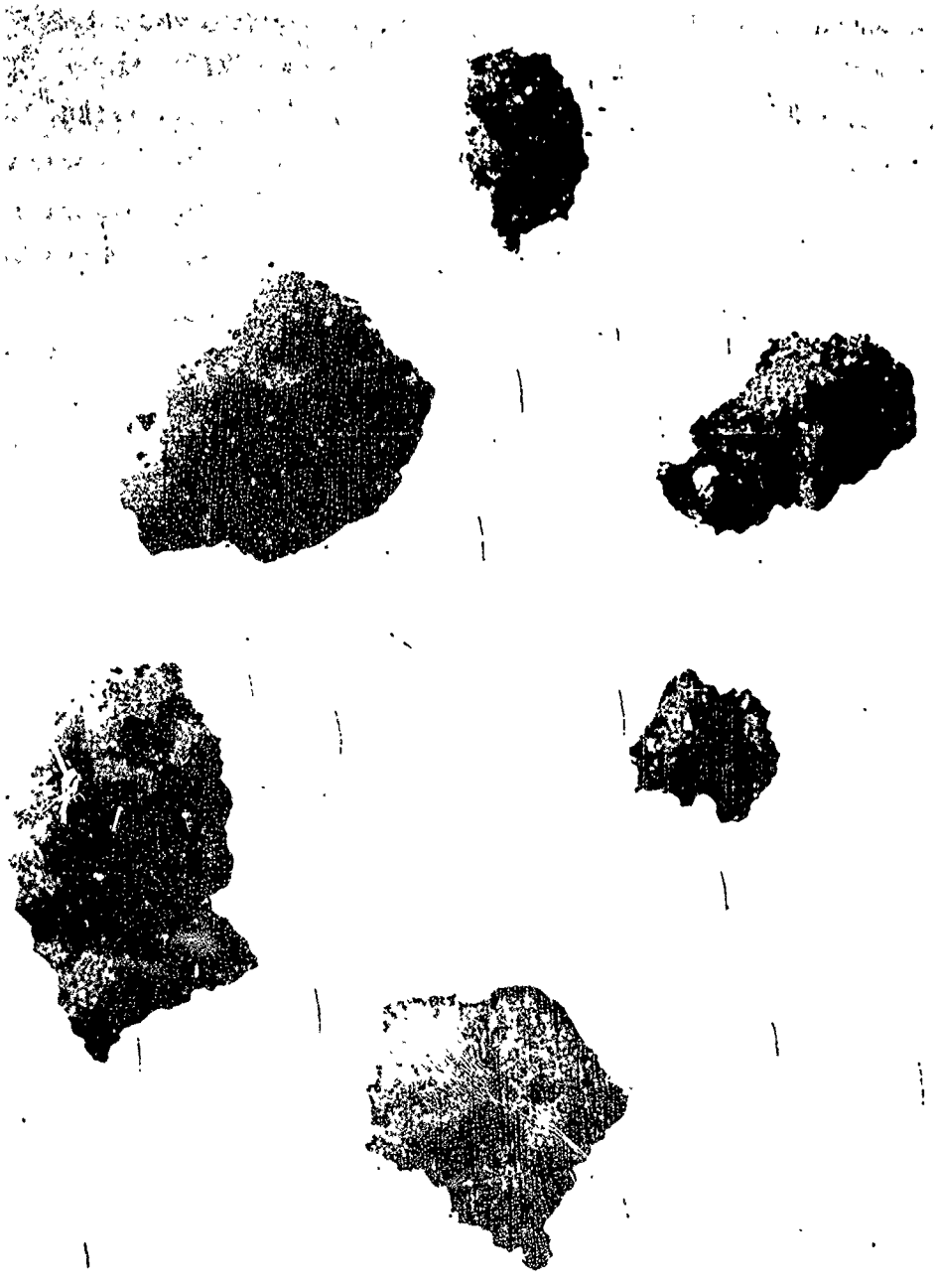

Figure 3. Tridymite Crystals (10-100 μm)

single, all the rhombohedral-faced crystals were single. All long rods were twinned on the $(10\bar{1}0)$ face. The prismatic crystals had a basic habit of $\{11\bar{2}0\} > \{12\bar{3}2\} > \{10\bar{1}0\}$ with infrequent small $(21\bar{3}1)$ faces. The rhombohedral-faced crystals had a dioptase habit with large $(11\bar{2}0)$ and smaller $(13\bar{4}1)$ faces (Fig. 4). A two-circle optical goniometer was used in making habit measurements, Laue back-reflection techniques were used in the x-ray identification and characterization, and a reflectometer was used in the identification of single or twinned crystals.

Needles and rods were observed to grow predominantely at both ends of the crystallization zone, whereas the more equidimensional crystals grew in the middle of the phase system. The various crystal phases and habits produced from different solute compositions are shown in Table 1. When the concentration of SiO_2 was increased, more equidimensional crystals were produced until, at a BeO/SiO_2 ratio of 0.3, only flat, badly formed, surface-nucleated phenacite was produced. With BeO/SiO_2 ratios below 0.2, only SiO_2 was produced. The optical quality of the phenacite crystals appeared to improve with increased SiO_2.

B. BROMELLITE AND TRIDYMITE

In the presence of SiO_2, synthetic bromellite was observed to grow primarily in three habits. When the concentration of SiO_2 was increased, ($BeO/SiO_2 = 3$), only a pyramidal habit was observed. These hemipyramids were of the form $\{10\bar{1}1\}$ with a truncated (0001) face and a complex curved $(000\bar{1})$ basal face. Very small prism $(10\bar{1}0)$ faces bounded the pyramid faces to the curved basal face. In all cases, the $(000\bar{1})$ had a twinned pyramid growing at the apex (Fig. 4). When the concentration of SiO_2 was decreased ($BeO/SiO_2 = 3.5$ to 14), the pyramid zone became smaller and the prism $(10\bar{1}0)$ zone became larger until, at a BeO/SiO_2 ratio of 14, prism rods with bounded curved $(000\bar{1})$ faces dominated. In pure BeO, only hexagonal plates, many single, and a few pyramids were observed. All crystals were 1 to 5 mm in size regardless of habit and were free of inclusions (Fig. 1).

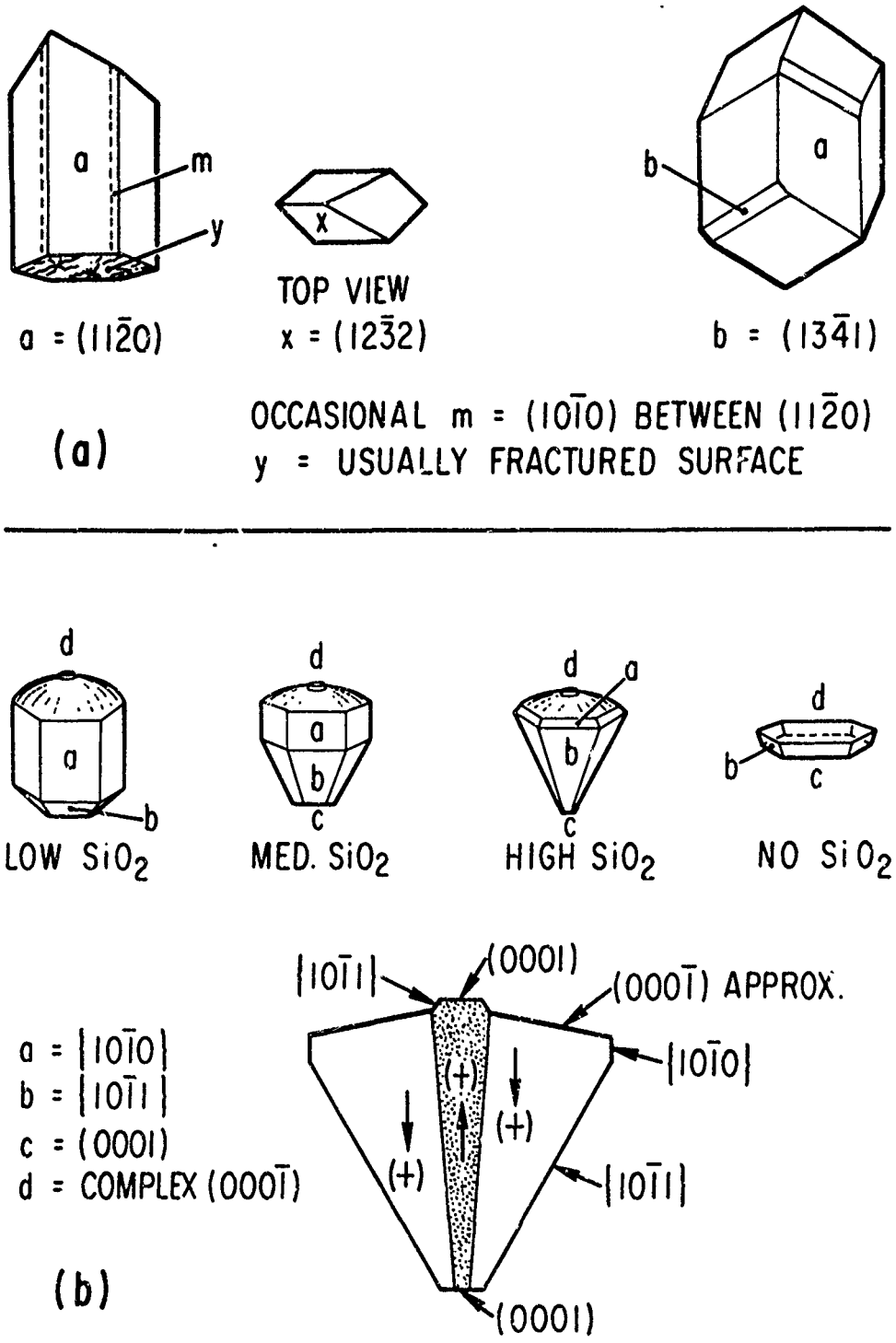

Figure 4. Phenacite and Bromellite Habit Modifications

a. Phenacite habit modifications due to twinning
b. Bromellite habit modifications with various SiO_2 doping

Table 1. Results of Crystal Phases (BeO, Be_2SiO_4, SiO_2) Grown in Li_2MoO_4 - 16 MoO_3 at 1165°C

Solute (BeO/SiO_2)	Results		
	SiO_2	Be_2SiO_4	BeO
0.1-0.2	Only	None	None
0.3	Mostly	Few flat surface crystals	None
0.4-0.7	Mostly	Needles, rods, few rhombs	None
0.8-1.5	Few	Mostly; needles, rods several rhombs	Few pyramids
2.0-3.0	None	Mostly; needles, rods, rhombs	More pyramids
3.5-5.5	None	Mostly; more equidimensional rods and more rhombs, few needles	Beginning curved $(000\bar{1})$ bounded by $(10\bar{1}0)$ prism
6.0-11.0	None	Few; more rods, needles and few rhombs	Mostly; more curved prisms, few pyramids, prism face getting larger
14.0	None	Few rods	Prism face larger than curved face; very few pyramids
15.0 (pure BeO)	None	None	Mostly flat hexagonal plates with very small $(10\bar{1}1)$ pyramid faces; a few pyramid crystals; no highly curved $(000\bar{1})$ faces

Solute = BeO + SiO_2 = 15 mole %

BeO/SiO_2 = variable

Flux = Li_2MoO_4 + MoO_3 = 85 mole %

Li_2MoO_4/MoO_3 = 5/80 = constant

High SiO_2 = phenacite rods and bromellite pyramids

Medium SiO_2 = phenacite equidimensional and bromellite small prisms with curved surface

Low SiO_2 = phenacite rods, a bromellite pyramid, and long prisms with curved surface

Pure BeO = flat hexagonal plates and few pyramids

Tridymite grew only as a by-product when the BeO/SiO_2 ratio was between 0.1 and 1.5. These crystals were small (10 to 100 μm) and grew in clusters (Fig. 3). When the Li_2O was increased (Li_2MoO_4-3.5 MoO_3), the crystals became larger (100 to 500 μm). The SiO_2 phase and composition were identified through x-ray diffraction techniques and spectrochemical analysis, respectively.

III. DISCUSSION

In these experiments, two very interesting effects were observed: the change in shape of phenacite from equidimensional to needle, and the habit change of bromellite from pyramidal to prism to platelet. In all runs, the dominate variable that affected crystal formation was the solute composition (BeO/SiO_2) because the temperature and flux composition were held constant.

A. PHENACITE

The crystals of Be_2SiO_4 in these experiments generally grew in three shapes: rods, equidimensional prisms, and rhombohedral faced. The rhombohedral-faced, equidimensional crystals grew untwinned and were fewer in number than the rods (up to 10 % of phenacite yield). More rhombohedral-faced crystals were observed at the center of the crystallization zone of phenacite than near the boundaries (Fig. 5).

The twinned crystals were all rod shaped, and the greatest number of twins were observed in the needle-shaped rods. Many reentrant faces were observed on the terminating ends of the needles. Needles dominated the yield at both ends of the crystallization zone, whereas more equidimensional crystals grew at the middle of the crystallization region.

These results indicated that the shape of the crystals was dependent on the availability of the Be_2SiO_4 molecules in the melt and the number of twins in each crystal. Fewer Be_2SiO_4 molecules were available at either end of the crystallization zone. This permitted the twinned phenacite to grow preferentially because of the many reentrant angles on the needle-shaped crystals. The terminating ends grew faster because faces with reentrant angles require less energy to grow. When a relatively large number of Be_2SiO_4 molecules occurred in the melt, equidimensional rod-shaped and rhombohedral-faced crystals were produced.

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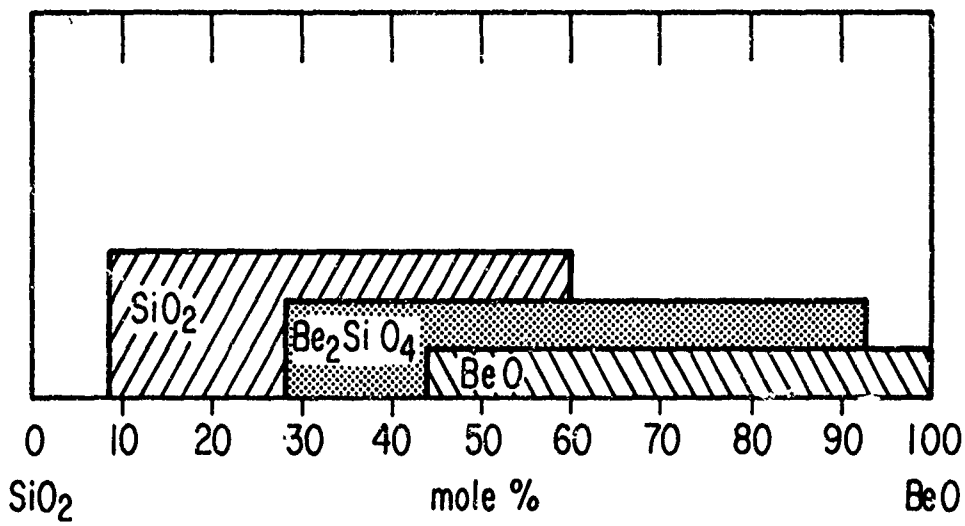

Figure 5. Phase Distribution of 15 mole % BeO-SiO_2, 85 mole % $Li_2MoO_4 \cdot 16\ MoO_3$ Grown at 1165°C.

In an earlier study,[6] a habit change from rods at temperatures below 1000°C to equidimensional rhombohedral-faced crystals above 1000°C was explained by solubility phenomena. At higher temperatures, more Be_2SiO_4 is dissolved. Therefore, more of these molecules nucleate and deposit on the slower growing rhombohedral faces. At lower temperatures, less Be_2SiO_4 is dissolved and the twinned rods preferentially use the Be_2SiO_4 molecules available.

In addition to the shape changes, other phenomena were also observed in the phenacite system. When the Li_2O concentration in the melt was increased, the crystallization region shifted further toward the BeO-rich side and decreased on the SiO_2 side of the zone. This was accompanied by a decrease in the crystallization of BeO and an increase in the SiO_2 yield. This decreased BeO yield is believed to be caused by the decreasing solubility and stability of BeO in Li_2O-rich melts. The decrease in the number of phenacite crystals for SiO_2-rich melts appears to be related to the formation of a lithium silicate ion, which decreases the availability of Be_2SiO_4 molecules. Tridymite had a small amount of Li^{+1} in its lattice that increased in proportion to increased Li_2O in the melt. Similarly, when Li_2SiO_3 was used as a source of SiO_4^{2-} in the melt, the size and yield of tridymite increased in SiO_2-rich melts whereas the phenacite decreased. Interestingly enough, the phenacite yield was greatest in runs in which quartz (SiO_2) rather than Li_2SiO_3 was used for a SiO_4^{2-} source.

Further, the crystals became enriched in high-order pyramidal faces when Li_2SiO_3 was used as a source of SiO_4^{2-} or when the melts contained large amounts of Li_2O. We believe that Li_2SiO_3 was a dominant SiO_4^{2-} bearing ion for these runs and was preferentially absorbed onto the pyramid faces, thereby slowing the growth rates. Indeed, for extremely fast growth runs, the pyramid faces became rough and had many small inclusions.

B. BROMELLITE

The occurrence of bromellite from melts enriched in SiO_2 is rather unusual in view of the earlier work of Newkirk and Smith,[1] who reported

that Be_2SiO_4 becomes the stable phase when as little as 0.1 wt% of the melt is SiO_2 for the Li_2O-rich systems. However, the presence of bromellite becomes reasonable when one considers that the solubility of BeO and its crystallization zone increases in proportion to increased MoO_3. Unfortunately, the phase diagram for this four-component system is not available. Therefore, it is difficult, if not impossible, to make generalizations regarding the crystals. However, a habit change (shape change) of the crystals was apparent and is described.

The BeO crystals grown from a pure Li_2O-MoO_3 melt were generally untwinned crystal (0001) platelets bounded by pyramid and prism faces. A few pyramid-shaped crystals were found in this run as well as in all runs with BeO + SiO_2. The crystals grown from a solute with a BeO/SiO_2 ratio of 14 were prism shaped with small pyramidal faces. These crystals were twinned with a polarity reversal twin terminating at the apex of a round $(000\bar{1})$ face (Fig. 4). At the apex of the pyramid, a flat (0001) face was formed. The pyramid faces were associated with the (0001) and the prism faces with the $(000\bar{1})$ face. The crystals became flatter in the $\langle 000\bar{1} \rangle$ direction as more SiO_2 was added to the melt, and the portion of the crystal with pyramid faces became equal to that with prism faces when the BeO/SiO_2 ratio was approximately 6. This process continued with increased SiO_2 until the pyramid faces became dominant at a BeO/SiO_2 ratio of 3. The crystal had a large curved $(000\bar{1})$, a small prism $(10\bar{1}0)$, a large pyramid $(10\bar{1}1)$, and a small (0001) face (Fig. 4).

This type of shape change was understandable when three basic assumptions were made regarding the crystal and the effect of SiO_2 on the crystal:

1. SiO_2 was preferentially absorbed onto the $(000\bar{1})$ face.
2. The portion of the crystal bounded by a pyramid face represented growth in the (0001) direction, and a prism represented growth in the $(000\bar{1})$ direction.
3. The appearance of reentrant angles on the face nominally designated $(000\bar{1})$ permited fast growth in this direction.

The change from platelet (pure Li_2O-MoO_3) to prism (low SiO_2) was caused by crystal twinning. Also, the change from prism to thick plate, with increased SiO_2, was caused by a decrease in the growth rate on the $(000\bar{1})$ face. Similarly, the crystal eventually became pyramidal shaped with continued decrease in growth rate in the $\langle 000\bar{1} \rangle$ direction. Throughout the process, the growth in the $\langle 0001 \rangle$ direction was not significantly affected.

In conclusion, the major factor in the shape change in bromellite was the growth rate in the $\langle 000\bar{1} \rangle$ direction. The pyramidal and prism faces are terminating faces and therefore their size was not dependent on the growth rate in the ±C direction.

IV. SUMMARY

Crystals of bromellite, phenacite, and tridymite were grown from Li_2MoO_4-MoO_3, and the twinning and shape-changing characteristics of bromellite and phenacite were studied. These growth characteristics were influenced by the presence of SiO_2, which also grew as the by-product tridymite. Nucleation and twinning were major factors in the shape change in phenacite, whereas growth in the ±C directions influenced the habit change in bromellite.

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