The Crystal Growth of Synthetic Fluor-phlogopite by the Moving Crucible Technique

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(Received January 18, 1965)

Fluor-phlogopite crystallizes from a melt with a composition corresponding approximately to the composition of mica, [$KMg_3AlSi_3O_{10}F_2$]. In the earlier stage of our experiments, the crystal growth of mica in the melt of a large mass was carried out and thus large mica crystals were obtained.1) A carbon granular resistance furnace was used for the melting and crystallization of mica. A batch of 30 kg. of a raw material mixture was heated in an aluminous clay or graphite crucible until a clear melt was obtained. The melt was then cooled at a cooling rate of 2 to 5°C per hour and left to cool to room temperature. The solidified mass was composed of interlocking mica crystals of various sizes. The maximum size of single crystals was about 5 cm. by 5 cm., but the yield of crystals of this size was small.

In order to increase the yield of large crystals in a given batch, it is necessary to prevent the formation of excess crystal nuclei at the beginning of crystallization and to give a preferred orientation to the growing crystals. Van Valkenburg and Pike2) used an elliptical crucible with a wedge-shaped bottom for the melting and crystallization of fluor-phlogopite. With a steep temperature gradient within the melt (larger than 50°C between the top and the bottom of the melt) and a slow rate of cooling (less than 1°C/hr.), a good development of the vertical and lateral orientation of mica crystals was obtained.

The Electrotechnical Experimental Station, Bureau of Mines,3) has developed an internal-electrical-resistance melting process for the manufacture of fluor-mica. This process can be used for the melting of a large quantity of a mica batch, but it usually results in the formation of a large number of interlocking crystals. Noda and Sumiyoshi4) used two sets of graphite electrodes placed vertically one over the other and thus obtained a development of the vertical orientation of growing crystals by changing the ratio of the electrical current passing through the upper and the lower parts of the mica melt with the internal-electrical-resistance melting process.

Daimon et al.5) applied the Kyropoulos (or Czockralski) technique of single-crystal growing to the crystal-growing of fluor-phlogopite, but they could not continue to grow crystals because of the change in the chemical composition of the surface layer of the melt caused by the evaporation of fluorine compounds.

Noda and Tsujimura6) used a stationary crucible technique of single crystal growing for fluor-mica single-crystal growing. The furnace used for the experiments had three platinum ribbon heaters placed at the bottom, the top, and the side of the furnace chamber, the electrical current of each heater being regulated separately. A platinum crucible containing the fluor-phlogopite batch mixture was placed in the chamber and heated to a temperature above the melting point of the mica. The average temperature gradients obtained by changing the electrical current of heaters ranged vertically from 10 to 80°C/cm., with the extreme temperature at the top. The fluctuation of temperature around the crucible could be kept within ±0.1°C by using fine alumina powder as a thermal insulator between the heaters and the crucible. A charge of 20 to 40 g. was melted and crystallized at a cooling rate ranging from 0.5 to 90°C/min. Mica crystals grew with their basal planes vertically parallel to the temperature gradient when the temperature gradient was larger than 40°C/cm. However, no lateral orientation was developed, and the breadth of the crystals was limited by the intersection of the neighbor crystals. Good crystals of a length equal to the depth of the melt were grown with an estimated rate of growth (the rate of the descent of the crystal-melt boundary) of less than 1 mm./hr. Sometimes a few crystals were observed to have grown to project above the surface of the melt.

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1) a) T. Noda, *J. Am. Ceram. Soc.*, **38**, 147 (1955); b) T. Noda and Y. Sumiyoshi, This Bulletin, **32**, 54 (1959).

2) Alvin Van Valkenburg and R. G. Pike, *J. Res. Nat. Bur. Standards*, **48**, 360 (1952).

3) R. A. Hatch, R. A. Humphrey and E. C. Worden, Synthetic Mica Investigations III. Report of Investigation 5283, Bureau of Mines, December, 1956.

4) M. Sumiyoshi and T. Noda, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 2069 (1960).

5) a) N. Daimon, *J. Ceram. Assoc. Japan* (*Yogyo Kyokaishi*), **60**, 179 (1952); b) N. Daimon, S. Shimizu, N. Ando and K. Kasuya, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **59**, 1335 (1956).

6) T. Noda and S. Tsujimura, ibid., **61**, 477 (1958).

With a given temperature gradient, the maximum depth of the melt is limited by the highest temperature, which is in turn limited by the furnace used. Also, too high a temperature should be avoided because of the increase in the evaporation of the fluorine compound from the melt. Therefore, the size of the grown crystals can not be made large when a large temperature gradient is required for the growing of single crystals with the stationary crucible technique.

Crystal Growth Without Seed Crystals

(Noda, Inagaki, Tanaka)

It is well known that the thermal history of melt affects the nucleation in the melt. In order to reduce the number of nuclei available for new crystal formation, the melt should be heated at a high enough temperature or for a long enough time for it to become a clear melt without any residual particles of raw material which may induce the nucleus formation.[7] On the other hand, when the melt is heated for an excessively long time or at too high a temperature, the melt cools, with a large undercooling which causes the sudden formation of a very large number of nuclei, once the nucleation begins.[8] Therefore, the control of the amount of nucleus formation needs a very delicate operation of the heating procedure.

Apparatus and Experimental Procedure.—The apparatus used for the moving crucible technique was a furnace the chamber of which was divided into two sections by a baffle plate.[9] The sections were heated by separate platinum-rhodium ribbon heaters in order to control the temperature of each room separately and in order to get a desired temperature gradient in the chamber. A charge of the fluor-phlogopite batch mixture was contained in a thin-walled platinum crucible 9 to 20 mm. in diameter, 20 to 30 mm. high, and with a conical bottom. The angle of the cone was 60°, and the apex of the cone was held on a platinum rod 5 mm. in diameter and 150 mm. long, the opposite end of which was in contact with the upper end of a stainless steel rod of the descending device. The crucible and the platinum rod were covered with refractory cases. The space between the crucible and the refractory case was filled with alumina powder so that no possible leakage of the batch melt might damage the wall of the furnace chamber.

The contact of the crucible apex with the platinum rod was designed to cool the apex preferentially by thermal conduction through the rod and to get so sharp a temperature gradient in the melt of the conical part of the crucible that the nucleation would take place only in the apex.

The rate of descent could be changed within the range of 0.1 to 1.0 mm./hr., because it was found from preliminary experiments that a rate of descent of 0.1 to 1.0 mm./hr. was good enough to grow single crystals of a good quality.

As raw materials, powdered fluor-phlogopite crystals or pre-melted blocks of fluor-phlogopite crystals were used. A crucible containing a charge of 20 to 300 g. of raw material was sealed by welding in order to prevent any change in the chemical composition of the charge by decomposition.

First, the crucible was placed in the upper section of the furnace; then the temperature of the furnace was raised. After the highest temperature of the furnace had reached about 1400°C, the temperature distribution in the furnace was measured and the crucible was moved to the position indicated as A in Fig. 1. In the figure the temperature distribution in the furnace is schematically described. The crucible was left there for a fixed time in order to complete the melting of the charge, and then it was manually moved to the position B, where the temperature of the crucible apex reached a definite temperature almost equal to or a little below the crystallization point of fluor-phlogopite (1375°C[8]). The crucible was

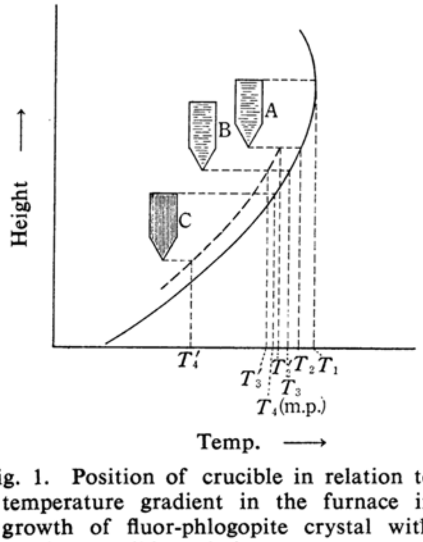

Fig. 1. Position of crucible in relation to the temperature gradient in the furnace in the growth of fluor-phlogopite crystal with the moving crucible technique.
—— Temperature of furnace
---- Temperature of apex of crucible

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[7] T. Noda and S. Sugiyama, ibid., **46**, 1082 (1943).

[8] S. Naka and T. Noda, ibid., **63**, 232, 777, 946, 950, 954, 1325 (1960).

[9] D. C. Stockbarger, "Crystal Growth," *Discussions Faraday Soc.*, **5**, 299 (1949).

TABLE I. EXPERIMENTAL DATA OF FLUOR-PHLOGOPITE CRYSTAL GROWTH BY MOVING CRUCIBLE TECHNIQUE WITHOUT SEED CRYSTALS

	Position A				Position B				
Exp. No.	Temp. of crucible apex	Holding time at T'_2	Furnace temp. at the level of crucible apex	$T_2-T'_2$	Temp. of crucible apex at the beginning of descent	Holding time at T'_3	Furnace temp. at the level of crucible apex	Rate of descent	Rate of* cooling of crucible apex
Series I	T'_2, °C	t_2, min.	T_2, °C	°C	T'_3, °C	t_3, min.	T_3, °C	mm./hr.	°C/hr.
50	1373	30	1423	70	1329	30	1389	0.75	2.0
54(A)	1355 1375	30 90	1409	34	1338	30	1368	0.75	2.0
55(A)	1350 1368	30 30	1413	45	1325	30	1378	0.75	1.7
57	1348 1362	30 15	1427	65	1338	30	1387	0.76	2.3
Series II									
44	1390—1380	90	1450	70	1340	120	1415	0.75	2.0
47	1360	10	1430	70	1308	110	1390	0.75	3.0
58	1345 1360	10 25	1430	70	1320	30	1380	0.80	—

* The rate of cooling was calculated from the rate of descent and the temperature gradient in the furnace by the following relation:

$$\text{Rate of cooling } (\Delta\theta/\Delta t) \fallingdotseq \text{Temperature gradient } (\Delta\theta/\Delta l) \times \text{Rate of Descent } (\Delta l/\Delta t)$$

where t is time, θ temperature and l distance.

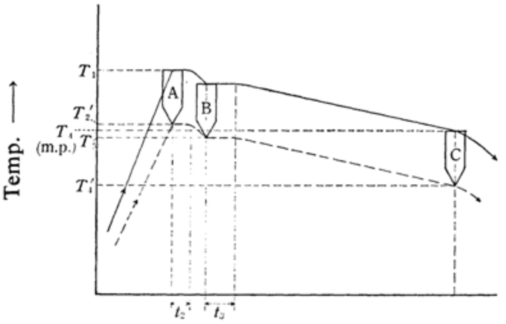


Fig. 2. Schematical heating program in the growth of fluor-phlogopite crystal with the moving crucible technique.

left there for a fixed time in order to form nuclei in the apex; then it was moved downward automatically at the rate of 0.75 mm./hr. The whole heating program is shown schematically in Fig. 2. When the top of the charge had passed the level of the crystallization temperature (the position C) and all of the melt was supposed to have crystallized, the furnace was cooled to room temperature. The temperature of the apex was measured by a thermocouple inserted between the crucible apex and the top of the platinum rod.

Results. — Some of experimental data are shown in Table I. When the apex of the crucible was placed directly on the platinum rod, the cooling effect of the rod was so large that the temperature of the apex was about 50—70°C lower than the furnace temperature of the same level. The temperature difference was reduced to about half (25—45°C) when a sintered alumina disk 1 mm. thick was inserted between the apex and the rod. The experiments with this inserted alumina disk are marked (A) in Table I.

In series I of the experiments, powdered crystals of fluor-phlogopite were used as raw material, while in series II of the experiments premelted blocks of fluor-phlogopite crystals were used. The premelted blocks were opaque white and were composed of minute, entangled crystals of mica.

In Exp. No. 50, in which the apex was held for 30 min. at the crystallization point of the mica, a very small number of unmelted crystals remained in the apex and a few single crystals of a good quality grew vertically from the apex to the top of the charge, orienting their basal planes parallel to the direction of growth, but without any lateral orientation (Plate I-1). Similar results were obtained with Exp. No. 55 (A) and 57, in which the apex temperature was held a little below the melting point of the mica (Plate I-2, -3). In Exp. No. 54, in which the apex was held for 90 min. at the crystallization point of mica, the resultant mass was composed of many randomly-oriented crystals (Plate I-4).

In Exp. No. 44, in which the apex was kept at 1390—1380°C for 90 min., the resultant mass was white, porcelain-like, and opaque, and was composed of a large number of minute

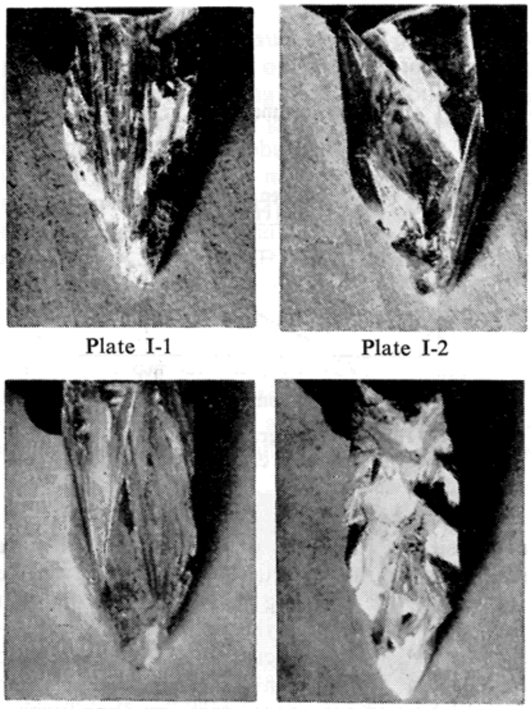


Plate I-1 Plate I-2

Plate I-3 Plate I-4

Plate I. Crystals grown by the moving crucible technique without seed crystals showing the effect of thermal history of melt.

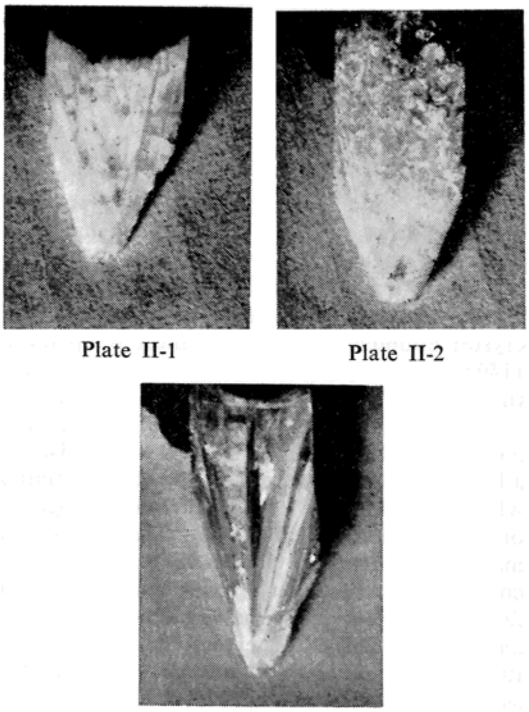


Plate II-1 Plate II-2

Plate II-3

Plate II. Crystals grown by the moving crucible technique without seed crystals showing the effect of thermal history of melt.

mica crystals and a small amount of needle crystals, probably chondrodite, all oriented vertically along the direction of growth (Plate II-1). In Exp. No. 47, in which the apex was kept a little below the crystallization point for a short time, small crystals remained at the apex; the size of the crystals deposited was small, but it became larger in the upper part of crucible, even though the apex was kept for 90 min. at 1300°C before the descent (Plate II-2). In Exp. No. 58, the thermal history of which was very similar to that of No. 57, single crystals of a good quality grew from the apex to the top of the charge (Plate II-3). This result was very similar to that obtained in Exp. No. 57. It can be seen from the similar results obtained in Exps. Nos. 57 and 58 that either powdered crystals or premelted crystalline aggregates can be used as raw material for the successful growing of fluor-phlogopite crystals.

As can be seen from the above experiments, the excessive heat treatment of the melt resulted in a large undercooling, which in turn resulted in the sudden formation of a large number of nuclei once the crystallization began. On the other hand, a number of seed crystals remained unmelted when the melting was insufficient. Experiments No. 54 and No. 44 are cases of excessive heat treatment, and Exp. No. 47 seems to be a case of insufficient melting, even though the apex was kept for a long time at a temperature a little below the crystallization point. Just to melt crystals down to the apex part may be the optimum

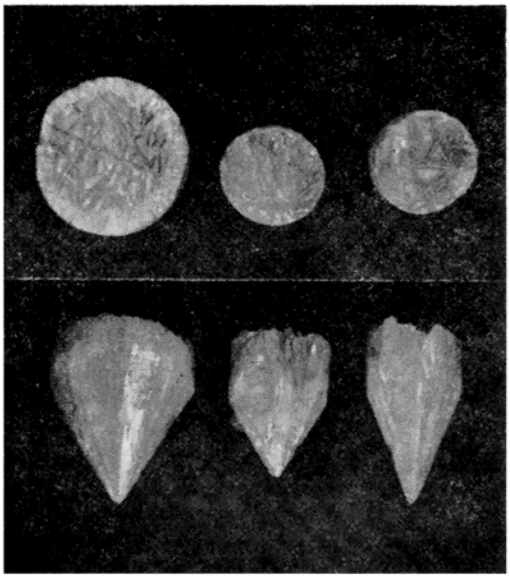


Plate III. Crystals grown by the moving crucible technique without seed crystals showing vertical and lateral orientation.

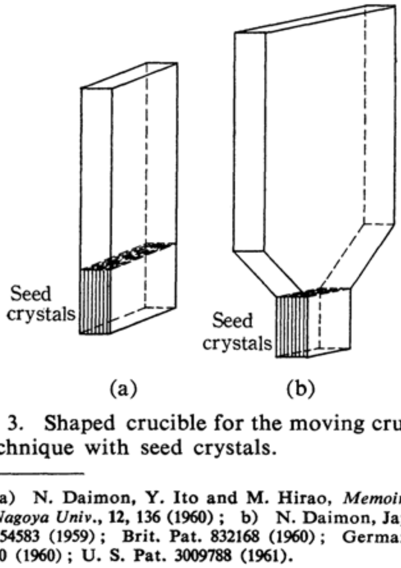
heat treatment for the growing of a few single crystals from the apex to the top of charge. This heat treatment can, however, be carried out only by a very careful control of the apex temperature. Experiments Nos. 50, 55 and 58 have heat treatments very close to the optimum.

With the moving crucible technique, the height of the charge is not necessarily as limited as it is with the stationary crucible technique, but the situation, in which the lateral orientation of grown crystals is random, is the same as with the latter technique. Some of the crystals grown by the moving crucible technique are shown in Plate III; they show a very good vertical orientation but a poor lateral orientation of crystal growth.

Crystal Growth Using Seed Crystals
(Daimon, Hirao, Amano)

One of the authors (Daimon) invented a technique of using parallel-packed sheets of fluor-phlogopite as seeds with the moving crucible technique for growing single crystals of fluor-phlogopite.[10]

As seed crystals, transparent, apparently flawless sheets were cut from fluor-phlogopite crystals which had been hand-splitted from crystal aggregates produced by the internal-electrical-resistance melting method. Platinum crucibles with square sections were made by welding platinum sheets 0.03 mm. thick by an oxygen-city gas torch. Several sheets of seed crystals were put together parallel to each other in order to make a book-like packet; they were then placed on the bottom in the crucible with their basal planes parallel to the vertical axis of the crucible, as is shown in Fig. 3. The raw material of fluor-phlogopite composition was put in the space over the seed crystals in the crucible, and the crucible was sealed by welding it in order to prevent the decomposition of the content. The crucible encased in a refractory sagger was placed in such a position in the furnace that when the highest-temperature part in the furnace was raised to 1400°C, the total charge of the raw material and the uppermost part of the seed crystals were to be melted. The temperature gradient across the crucible at the beginning of the descent is shown schematically in Fig. 4.



(a) (b)

Fig. 3. Shaped crucible for the moving crucible technique with seed crystals.

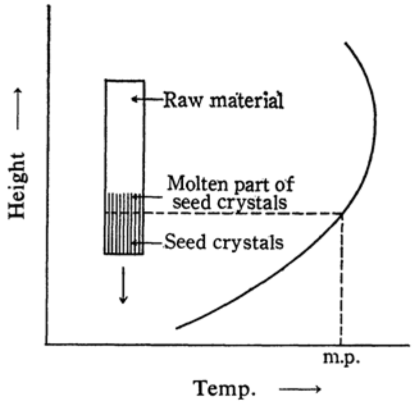


Fig. 4. Temperature gradient across the crucible in the moving crucible technique with seed crystals.

The sagger was connected with a descending device, the rate of descent being varied from 0.4 to 35 mm./hr. The temperature of the highest-temperature part in the furnace was kept at 1400°C during the descent. The temperature gradient around the crystal-melt boundary was estimated from the temperature difference between 1400°C and 1375°C, the crystallization point of fluor-phlogopite, divided by the distance between the seed crystal-grown crystal boundary and the highest temperature (1400°C) level in the furnace. The temperature gradient varied from 60 to 10°C/cm.

Powdered crystals of fluor-phlogopite, pre-melted blocks of fluor-phlogopite crystals, and a batch mixture of chemicals the composition of which corresponded to that of fluor-phlogopite or its pre-melted blocks were used as raw materials. When a batch mixture of an off composition was used, the concentration of fluor-phlogopite in the melt gradually decreased and, consequently, the crystallization temperature of fluor-phlogopite gradually decreased,[11] as the crystallization proceeded. This situation is in general not favorable for the growth of single crystals in the melt.

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[10] a) N. Daimon, Y. Ito and M. Hirao, *Memoir. Fac. Eng. Nagoya Univ.*, 12, 136 (1960); b) N. Daimon, Japanese Pat. 254583 (1959); Brit. Pat. 832168 (1960); German Pat. 1088940 (1960); U. S. Pat. 3009788 (1961).

[11] T. Noda, *J. Am. Ceram. Soc.*, 38, 147 (1955).

As the result of a number of growing experiments,[12,13] the optimum temperature gradient in the growing zone was found to be about 40°C/cm. and a good, clear "booklet" of mica crystals was obtained with the rate of descent of 1.0 to 0.4 mm./hr. (Plate IV). It seems that better crystals may be grown with a smaller rate of descent. A booklet as large as 10 cm. × 5 cm. × 1 cm. was grown in the authors' laboratory.[14] (Plate V)

Synthetic fluor-phlogopite has been reported to have a monoclinic monolayer (1 M) structure. The optical angles (2V) of the mica reported range from 0 to 14°.[15-18] The results of the measurement of a large number of both seeds and grown crystals of fluor-phlogopite showed that the optical angles were distributed in the range from 0 to 16°, with a maximum distribution at angles less than 9 and around 15°. The optical angles of the grown crystals were mostly the same as those of their seed crystals; only a few had smaller or larger angles than those of their seeds.[13]

Weissenberg X-ray photographs of the single

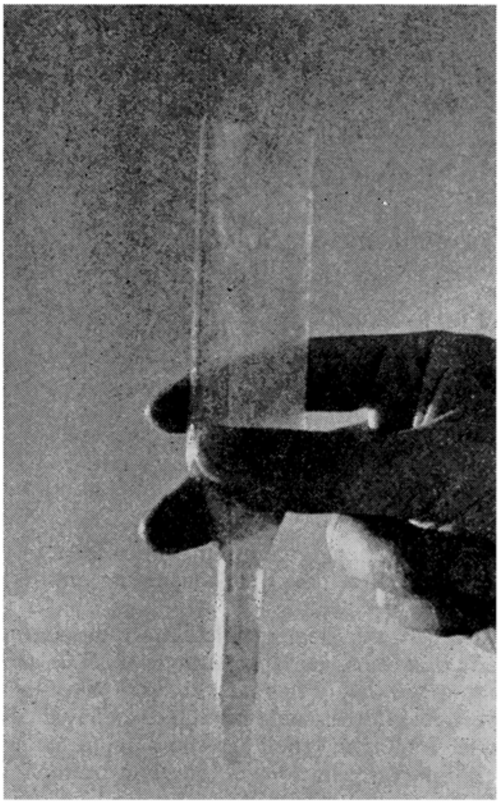


Plate IV. A booklet of fluor-phlogopite crystals grown by the moving crucible technique with seed crystals.

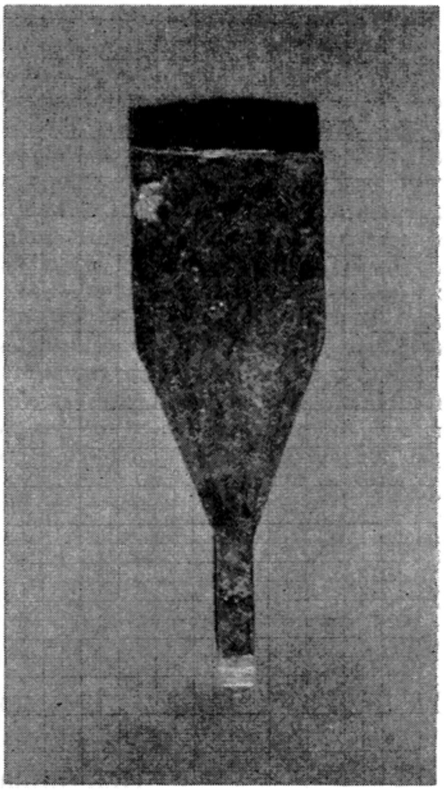
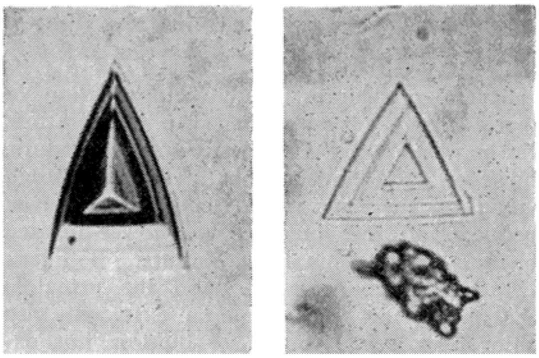


Plate V. A booklet of fluor-phlogopite grown by the moving crucible technique with seed crystals; length 14 cm., width 5 cm., thickness 1 cm.



(a) (b)

Plate VI. Etch figures of fluor-phlogopite crystals.
(a) 1 M type (b) Polysynthetic type

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[12] N. Daimon, Y. Ito and M. Hirao, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 1530 (1961).

[13] N. Daimon and T. Amano, ibid., **65**, 507 (1962).

[14] N. Daimon, *Electronics* (*Erekutoronikusu*), **6**, 126 (1961).

[15] H. S. Yoder and H. P. Eugster, *Geoch. Cosmoch. Acta*, **6**, 157 (1954).

[16] J. A. Kohn and R. A. Hatch, *Am. Mineral.*, **40**, 10 (1955).

[17] J. V. Smith and H. S. Yoder, *Mineral. Mag.*, **31**, 209 (1956).

[18] S. Naka and T. Noda, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 232 (1960).

crystal of fluor-phlogopite with an optical angle around 14° showed the 1 M symmetry, while that of the crystal with an optical angle of less than 9° gave reflection spots which could be interpreted by the polysynthetic-twin model.[19]

By etching fluor-phlogopite crystals with gaseous hydrogen fluoride or its concentrated aqueous solution, isosceles trianglar etch pits were observed on the surface of crystals with optical angles around 15° (Plate VI-a) and apparent equilateral trigons (Plate V-b) on the surface of crystals with optical angles of less than 9°, corresponding to the 1 M and polysynthetic twin-type structure respectively.[20]

The etch pit concentration of crystals grown at a smaller rate was smaller than those grown at a larger rate; for example, the etch pit concentration of crystals grown at the rate of 1.5 mm./hr. was $0.3-0.5\times10^4/\text{cm}^2$, about half that of crystals grown at the rate of 13 mm./hr. The etch pit concentration of seed crystals, which were produced by the internal-electrical-resistance melting method, was about the same as those grown at the rate of 13 mm./hr.[21]

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[19] T. Amano and N. Daimon, ibid., **66**, 1416 (1963).
[20] N. Daimon and T. Amano, ibid., **67**, 1860 (1964).
[21] N. Daimon and T. Amano, ibid., **67**, 1865 (1964).