*Experiments on Synthetic Mica Crystal Growing. Crystal Growing with Carbon Granule Resistance Furnace**

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In experiments on the growing of synthetic fluor-phlogopite, it is necessary first to melt the mixture of raw materials of fluor-phlogopite composition to a clear liquid by heating it at about 1450°C and then to maintain the resultant melt for many hours at temperatures within a range of several tens of degrees around its crystallizing temperature of about 1350°C. For the growing of large crystals, the melt should be cooled very slowly.

The rate of cooling necessary for the growing of large crystals may be acquired in two ways.

1) For small melts, by precise control of the temperature of the melt; 2) by using a large enough quantity of melt to obtain the necessary rate through natural cooling or by less precise control of temperature. A large mass of melt will provide sufficient space for growing large crystals.

The first way may be carried out by applying the technique originally designed by Stöber[1], Bridgman[2] and Kyropoulos[3] for growing large single crystals, techniques which have been used in the manufacture of optical crystals. The results of experiments done along this line will be reported later; experiments on growing synthetic mica crystals in large melts are described in the present paper.

* Summary of papers published in *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zasshi*), **59**, 352, 1323 (1956); and *J. Ceram. Assoc. Japan.* (*Yogyo Kyokai Shi*), **64**, 95 (1956).

1) F. Stöber, *Z. Krist.*, **61**, 299 (1925).

2) P. W. Bridgman, *Proc. Am. Acad. Arts. Sciences*, **60**, 303 (1925).

3) S. Kyropoulos, *Z. anorg. Chem.*, **154**, 308 (1926); *Z. Phys.*, **63**, 849 (1930).

Experimental

Apparatus.—Among various types, platinum resistance, silicon carbide resistance, carbon resistance and gas-fired furnaces may meet the requirements for the temperature range for synthetic mica crystal growing. In small-scale experiments, the first two types of furnace were used. In large-scale experiments, however, carbon granule resistance furnaces, designed especially for this purpose, were used. Because, the platinum resistance furnace being excluded for its prohibitive expense, a silicon carbide resistance furnace was unexpectedly found to serve only a short time, as heating resistors were attacked by fluorine-containing vapor evolved from the melt.

The first requisite was to design and construct a carbon granule resistance furnace having all the characteristics needed to meet the requirements of temperature control necessary for synthetic mica crystal growing, because this type of furnace is usually considered inadequate for precise temperature control and the furnace is apt to have a reducing atmosphere.

As a preliminary step in designing the furnace, characteristic data, such as electric power input per unit surface area of heating zone, specific resistance of carbon granule heating element, and power input per unit volume of carbon granule heating element, were investigated by a critical examination of several commercial furnaces of the carbon granule resistance type.

A furnace of 2 kg. melting capacity of this type was constructed, employing these characteristic data as a design basis, and used for medium scale experiments on synthetic mica crystal growing. Then based on a close examination of both calculated and observed characteristic data of this furnace, a furnace of carbon granule resistance type having a 30 kg. melting capacity was constructed for large-scale experiments on synthetic mica crystal growing. The furnace

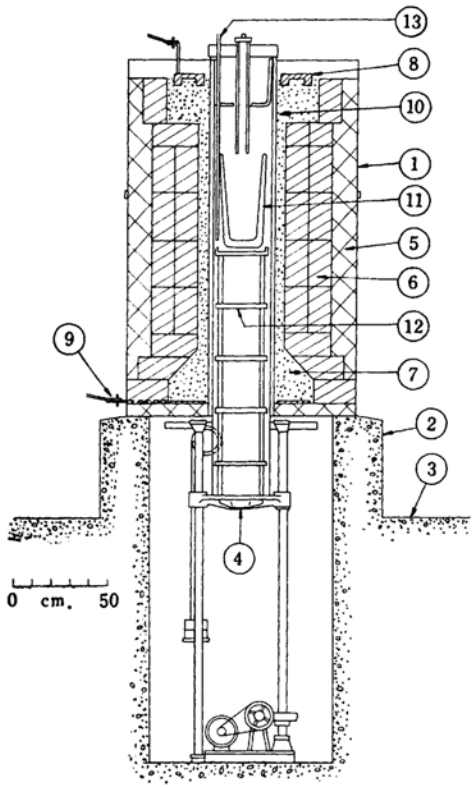


Fig. 1. Carbon granule resistance furnace.

1: Steel case 2: Concrete foundation 3: Floor 4: Motor-driven lift 5: Heat insulator 6: Refractories 7: Carbon granule resistance 8: Upper electrode 9: Lower electrode 10: Core tube 11: Clay crucible 12: Buffer plate 13: Thermocouple protection tube
Inner dia. of core tube 30 cm., Outer dia. of core tube 34 cm., Width of heating element 6 cm., Height of heating element L 110 cm., Sectional area of heating element A 154 cm^2, L/A 0.15_9 cm^{-1}, Volume of heating element V 82.9 l,
Specific resistance of carbon granule resistor
ρ 1.44 Ω cm. (room temp.)
0.50_6 Ω cm. (at 1675 °C),
Total resistance of heat element R
0.21_6 Ω (room temp.) 0.07_8 Ω (at 1675 °C),
Surface area of heating zone A_i 104 dm^2,
Power input per unit surface area of heating zone EI/A_i
0.09_6 kW./dm^2 (room temp.)
0.38_4 kW./dm^2 (1675 °C),
Total input EI
10 kW. (room temp.) 40 kW. (1675 °C),
Power input per unit volume of heating element EI/V
0.12_0 kW/l (room temp.) 0.46_2 (1675 °C),
Current I 215 amp. (room temp.)
720 amp. (1675 °C),
Terminal voltage E 46.5 V. (room temp.)
55.8 V. (1675 °C),

was remodeled several times in the process of the research and a sectional sketch of the furnace in its final form is given in Fig. 1, with its characteristic data.

The power input (P) for heating the furnace up to a certain temperature and the power input (P') for keeping the furnace at that temperature are related to temperature (θ), the effective surface area of heating zone (a), and the time (t) required for heating the furnace up to the temperature by the following equations[4]:

$$P = ca^{0.9}\theta^{1.55}t^{-0.5} \quad (1)$$

$$P' = c'a^{0.9}\theta^{1.55} \quad (2)$$

For this furnace, the values of c and c' were found to be 76 and 7.5 respectively. The power input for keeping the furnace at 1350°C was about 20 kW, the heat loss at the furnace side wall being about 65% of total input, and at the top and the bottom of the furnace, about 35%.

The furnace was harnessed with two voltage regulators in sequence, i.e. a motor-driven induction regulator, controlled by an electronic controller, was used with a saturable reactor combined with a magnetic amplifier and a D.C. voltage stabilizer. With this device, the temperature of the furnace could be controlled within ±2~3°C in the temperature range of 1300° and 1400°C by regulating the terminal voltage within ±0.05%.

A motor-driven lift was attached under the furnace, so that a crucible placed on the lift could be raised to a predetermined height in the furnace.

Raw Materials.—Raw materials, such as quartzite, alumina, magnesia, talc and potassium silicofluoride, were of commercial grade except the poassium carbonate which was of chemical grade. These materials were analysed and were found to have sufficient purity for the present purpose. All gradients of these raw materials were taken into account in calculating the mixing ratio of the raw materials for the preparation of batch mixtures.

Because the loss of fluorine due to decomposition of fluoride in the batch during heating is accelerated by the presence of water vapor[5], the mixture of calculated amounts of silica, magnesia, talc, alumina and potassium carbonate was first calcined at about 1000°C to expel water and carbon dioxide contained in the mixture and then the calculated amout of potassium silicofluroride was added.

Batches of POM 2 composition were used in most of the experiments of the present series because it was found, from results of experiments on the determination of crystallizing

4) T. Hayashi, *J. Electrochem. Soc. Japan, (Denki Kagaku)*, **15**, 55 (1947).
5) a. V. Middel, PB 32546 (1947); b. R. A. Hatch and R. A. Humphrey, *Office of Naval Research* (1950), The Synthetic Mica Program 2; c. A. Van Valkenburg and R. G. Pike, *J. Res. Natl. Bur. Stand.*, **48**, 360 (1952); d. W. Eitel, R. A. Hatch and M. V. Denny, *J. Amer. Ceram. Soc.*, **36**, 341 (1953).

temperature of fluor-phlogopite[6] and also from results of a large number of crystal growing experiments[7], that this composition was one of the most favorable compositions for crystal growing. Two examples of batch mixtures are given in Table I.

TABLE I

	POM 2 composition %		Batch mixture I %	Batch mixture II %
SiO_2	40.58	Alumina	11.72	11.30
Al_2O_3	11.60	Talc	60.29	48.07
MgO	27.32	Magnesia	5.88	10.51
K_2O	10.79	Potassium silicofluoride	18.38	18.77
F	9.71	Potassium carbonate	3.73	2.35
		Quartzite		7.61

Experimental Procedure.—The evaporation of fluorine in the batch is highest in the course of reaction during heating above 1000°C and is comparably low in the molten state. Therefore, it was planned to melt the batch as quickly as possible to minimize the evaporation of fluorine.

At first it was our plan to follow the melting procedure in this way, viz: the crucible containing the batch is placed in a low position within the furnace (c.f. Fig. 1), heated up to about 1000°C, and then moved to a higher temperature region which had already been heated to 1400°C. After completion of the melting, the crucible is raised or lowered to ensure the required temperature difference between the top and the bottom of the crucible and then cooled slowly by controlling the power input of the furnace. The heating and cooling curve of the experiment carried out in this way is shown in Fig. 2.

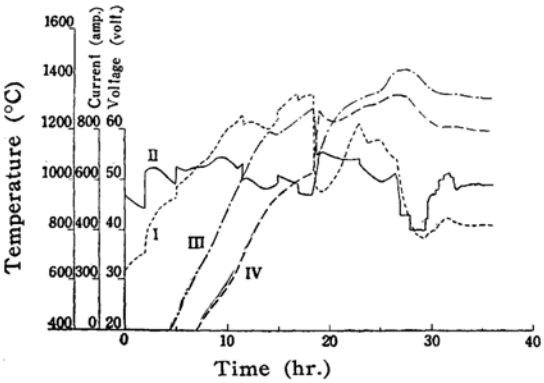


Fig. 2. Heating and cooling curve of experiment No. 1.
I: electric current
II: terminal voltage
III: temperature at the top of the crucible
IV: temperature at the bottom of the crucible

This procedure was abandoned because of operational difficulties, such as failure to get the crucible, buffer plates, thermocouple protecting tube and other furnace furnitures on the lift to raise smoothly, and the increase of undesired updraft of cold air during and after the raising operation. Most of the experiments were carried out in the following way. An unfilled crucible is first placed in the furnace; then the furnace is heated by passing electric current through the resistance element. After the temperature has reached about 1400°C, the crucible is charged several times with the batch until it is filled with the melt. Upon completing the charge, the crucible is covered with a lid, the temperature of the crucible is maintained above 1400°C for 5~6 hours to obtain the clear melt, and then cooled slowly by controlling the power input of the furnace.

Because well-sintered high-aluminous clay crucibles used in the earlier stages of this series of experiments were found to be less resistant to thermal shock, calcined but unsintered high-aluminous clay crucibles were used in later stages of the series. They were first heated in the furnace up to 1650°C to sinter. After the sintering, the temperature of the furnace was lowered to about 1400°C, the crucible was charged with the batch material and after completion of the melting, the melt was cooled slowly, as described above. The heating and cooling curve of a typical experiment of this series is given Fig. 3.

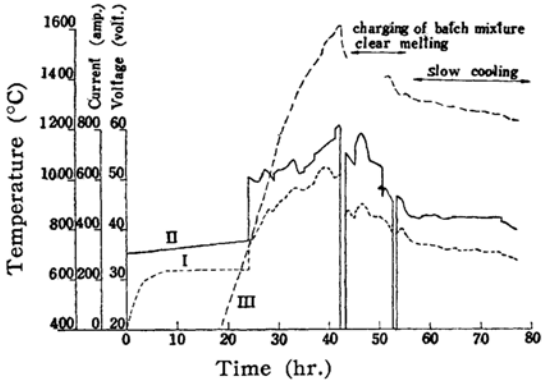


Fig. 3. Heating and cooling curve of experiment No. 13.
I: electric current
II: terminal voltage
III: temperature at the bottom of the crucible

Crucible Material.—Graphite and high-aluminous clay crucibles were used in the experiments because graphite was known not to be wetted and corroded by the melt, and a well-sintered alumina or high-aluminous clay body

6) T. Noda and S. Sugiyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zasshi*), **46**, 1082 (1943); cf. T. Noda, *J. Amer. Ceram. Soc.*, **38**, 147 (1955).
7) T. Noda, *Industrial Physical Chemistry* (*Kogyo Butsuri Kagaku*), No. 1, 108 (1948); cf. T. Noda, This Bulletin, **23**, 40 (1950).

was found to resist the corrosion[8].

Graphite crucibles used were cylindrical in shape, 25 cm. in outer diameter, 50 cm. in height and 46 cm. in depth. The crucible was placed in a sagger made of fire clay, with grog powder packed in the intersticial space between the crucible and the sagger, thus preventing the oxidation of graphite. Buffer plates and cylinders made of fire clay were placed on and under the sagger in the furnace in order to decrease unfavorable convection current in the furnace.

Mica aggregates which crystallized in graphite crucibles were gray, minute carbon particles deposited in interstitial glass between mica crystals discoloring them. Crystals grown in graphite crucibles were generally small, and even when they grew large, they were mostly of mosaic nature.

It seems that one of the causes of small crystal formation is that the wall of graphite crucible is not wetted with the melt and consequently the wall does not initiate the nucleation of mica, so that the melt tends to become supercooled and forms a large number of nuclei when it starts to crystallize at a supercooled temperature.

In one experiment with graphite crucible, the molten state was maintained down to a temperature of about 150°C below the crystallizing temperature and small mica crystals rapidly formed around a steel wire when it was quickly dipped into the melt, while glass adhered to a wire quickly dipped into a melt in a high-aluminous clay crucible.

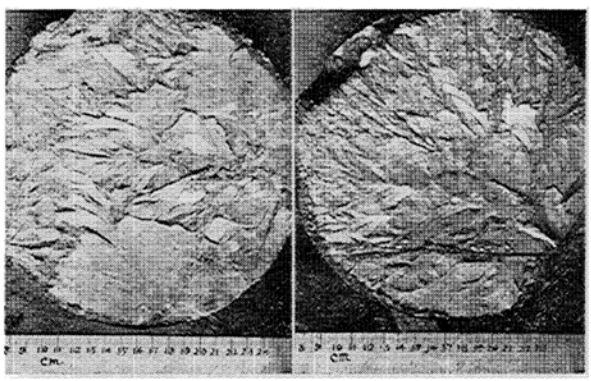
These observations suggest that the melt in graphite crucible was in a supercooled state or was in a state of easy crystallization with slight stimulus. Another suspected cause for small crystal formation was that a change in chemical composition of the melt was accelerated by the reducing atmosphere, but the change was not verified by chemical analysis. Also, the presence of minute carbon particles might stimulate the nucleation, although no positive assertion can be made.

High-aluminous clay crucibles used in the experiments were of alumina and silica, about 50% each. Crucibles sintered at about 1600°C or below were heavily corroded by the melt, so that the thickness of crucible wall decreased to about one-half of its original thickness, changing the chemical composition of the melt markedly and often leaking the melt completely.

Crucibles sintered at about 1650°C were found to withstand corrosion of the melt. The wall of clay crucibles initiated the nucleation of mica crystals, so that in the earlier stage of crystallization, large numbers of small crystals were formed in the vicinity of the wall. However, in the course of slow cooling, some of these crystals or crystal nuclei which were spontaneously formed in the melt grew to large single crystals of good quality. Mica aggregates crystallized in clay crucibles were slightly colored brown owing to iron contamination coming from crucible material. These aggregates contained a slightly larger amount of glass than those crystallized in the graphite crucible, but contained no carbon.

Result

Temperature Gradient in Melt and Oriented Growing of Crystals.—The formation of large crystals grown horizontally in the surface layer of melt was often observed when the temperature difference between the top and the bottom of the crucible was small during the crystallization period. Crystals grown in this way are shown in Fig. 4a. The crystal in the lower part of the figure measured 7 cm. by 12 cm. and was slightly curved. The evaporation of potassium and fluorine from the surface of the melt must have caused the crystallizing temperature of the surface layer of the melt to become higher and the early-formed crystals in this layer may have been in contact with the melt and may have had a longer time to grow than crystals formed later in the bulk of the melt. This may be the reason for small crystals growing at random in the bulk of the melt in spite of the formation of large crystals in the surface layer. Crystals grew upwards from the bottom of the crucible when the bottom temperature was sufficiently lower than the top temperature to cause the crystal nuclei to form originally at the bottom of the crucible. Edges of basal planes of vertically grown crystals can be seen on the surface of the crystalline mass shown in Fig. 4b. Rapid cooling causes new crystal nuclei to form in a slightly displaced direction from the orientation of



(a) (b)

Fig. 4. Top view of crystallized mass

8) T. Noda and M. Konno, *J. Ceram. Assoc. Japan*, (*Yogyo Kyokai Shi*), **57**, 25 (1949); T. Noda and K. Mori, ibid., **57**, 104 (1949); T. Noda and T. Ikenoue, ibid., **57**, 163 (1949).

TABLE II
TEMPERATURE GRADIENT AND ORIENTED CRYSTAL GROWING

Experiment	Height of melt cm.	Temperature difference °C	Temperature gradient °C/cm.	Oriented growing
5	30	10	0.3	none
6	30	40～150	1.3～5	slight
8	30	115	3.8	slight
9	30	150	5	noticeable

the original crystals. This type of formation results in curved crystals of mosaic nature and under the most unfavorable conditions in dendritic crystals which are manifested by the branched edges of basal plane, as seen in Fig. 4b.

For the purpose of obtaining the relationship between the temperature gradient in the melt and the oriented growing of crystals, the temperature difference between the top and the bottom of the crucible and the qualitative degree of oriented crystal growing are given in Table II.

Although temperature readings with thermocouples placed at the top and bottom level of the crucible may not always indicate true temperatures of the melt at the same levels, the temperature gradient calculated by dividing the temperature difference by the depth of melt may, for practical purposes, be used for deduction of the experimental result. It can be seen from data of Table II that no oriented growth of crystals was observed when the temperature gradient was 1～2°C /cm. and that the temperature gradient of 4～5°C/cm. may be needed for oriented growth.

Rate of Growth and Quality of Crystal. —In one experiment in which the temperature at the bottom was higher than that at the top, a steel wire was frequently dipped into the charge contained in a graphite crucible to see the start of crystallization. When the temperature was 1230°C at the top and 1375°C at the bottom, the charge was in the molten state; when the temperature was 1205°C at the top and 1335°C at the bottom, a part of the charge began to solidify, the main part being a viscous melt; the crystallization was completed when the temperature was 1185°C at the top and 1325°C at the bottom. Because of the inverted temperature gradient, the convection may have occurred in the melt to equalize the temperature difference, so the real temperature of the upper layer of the melt may have been higher than the measured value. However, a considerable temperature gradient may still have been held, because crystals grew vertically downward from the upper layer. The crystallizing temperature of the melt was estimated to be about 1350°C, while in the above case the actual crystallization began between 1325°C and 1205°C.

This means that a great supercooling took place. It seems that a rapid rate of cooling may favor the occurrence of supercooling. Therefore the melt does not always begin to crystallize when the temperature of the melt is cooled to that corresponding to its crystallizing temperature, and the rate of cooling of the melt, calculated by dividing temperature-drop in the slow cooling period by the duration of slow cooling, does not necessarily correspond to the true rate of cooling during the crystallization. However, in the course of slow cooling, a slow-down of the cooling rate due to the generation of the heat of crystallization* was generally observed, and it can be assumed that the period of the slow-down of the cooling rate corresponds to the duration of crystallization. Therefore the rate of crystal growth of basal plane can be calculated by dividing the size of the largest crystal found in the solidified mass by the duration of crystallization, assuming that the crystal had grown throughout the duration of crystallization, although the solidified mass in the crucible was usually composed of a large number of crystals of various sizes. The rate of crystal growth thus calculated and the quality of crystals produced are given in Table III.

In experiment No. 13, using a well-sintered high-aluminous clay crucible, several clear single crystals measuring about 5 cm. by 5 cm. could be split from the solidified mass, although the yield of crystals of this size was very small. Two of these crystals are shown in Fig. 5. In this experiment, the rate of cooling was 2～5°C/hr.. The quality of these crystals is designated in Table III as "excellent". Crystals which are not perfect

* 74±3 cal./g., N. Daimon, T. Horibe, K. Mukumoto and T. Noda, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zasshi*), 55, 762 (1952).

TABLE III

RATE OF CRYSTAL GROWTH AND QUALITY OF CRYSTAL

Exp. No.	Crucible used	Crystallization time hr.	Cooling rate °C/hr.	Largest crystal cm.	Crystal growth rate mm./min.	Quality of crystal
5	Graphite	21	2～ 5	10	0.08	good
6	〃	17	3～20	13	0.13	poor
8	〃	2	rapid cooling	5	0.42	very poor
9	〃	2	15～20	3	0.25	poor
13	High aluminous clay	13	2～ 5	5	0.06	excellent

TABLE IV

CHEMICAL COMPOSITION OF BATCHES AND PRODUCTS

Exp. No.		MgO %	SiO_2 %	SiO_2 %mod*	SiO_2 Δ%**	Al_2O_3 %	Al_2O_3 %mod*	Al_2O_3 Δ%**	K_2O %	K_2O %mod*	K_2O Δ%**	F %	F %mod*	F Δ%**
11	batch	27.64	42.92			12.16			11.43			9.93		
	product	27.03	43.74	44.74	+1.84	13.61	13.92	+1.76	10.42	10.65	−0.78	9.33	9.54	−0.39
12	batch	26.84	41.07			12.58			11.26			9.46		
	product	26.75	43.79	43.92	+2.85	14.98	15.02	+2.50	9.71	9.74	−1.52	8.09	8.11	−1.35
13	batch	27.35	39.19			15.43			11.07			9.50		
	product	24.14	43.02	48.74	+9.55	17.21	19.57	+4.41	10.65	11.96	+0.90	8.11	9.19	−0.31

* %mod = (% in product) × (MgO % in batch)/(MgO % in product)

** Δ% = (%mod) − (% in batch)

single ones, but are of mosaic nature are designated as "poor" in quality. When they were split from the solidified mass, these crystals separated into many small ones. Crystals grown at a rate higher than 0.1 mm./min. were always imperfect mosaic crystals. It can be deduced then that in order to grow good single crystals which can be split from the solidified mass, the rate of growth should be less than one-tenth of a millimeter per minute.

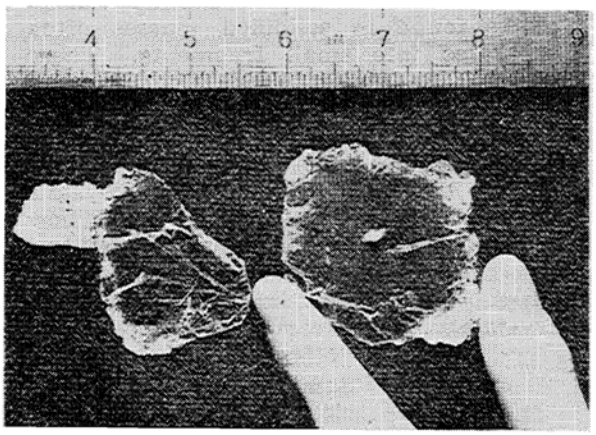


Fig. 5. Single crystals of fluor-phlogopite.

Change in Chemical Composition of Charge during Process.—Chemical compositions of batch mixtures and solidified products of three experiments are given in Table IV.

We used in experiment No. 11, a slightly-sintered high-aluminous clay crucible for melting for a relatively short period, in experiment No. 12, a slightly-sintered high-aluminous clay crucible for a long period and, in experiment No. 13, a well-sintered high aluminous clay crucible for a long period. Changes in individual components of the charge during the melting were calculated on the assumption that the content of magnesia was kept constant because no magnesia came from the crucible and the evaporation of magnesium fluoride was negligible.

In experiment No. 11 where the short period melting and the rapid cooling were used, small crystals resulted without remarkable change in the chemical composition of the melt. In experiment No. 12, the clay crucible was heavily corroded. This resulted in a considerable increase in content of alumina and silica. The loss of fluorine and potassium due to the evaporation was also remarkable. The great shift of the chemical composition and especially a remarkable deficit of fluorine in the melt, may be to blame for the formation of small crystals. The well-sintered clay crucible used in experiment No. 13 strongly resisted the corrosion of melt. The slow-cooling procedure was carried out as planned and the solidified mass contained many large crystals, as described above. The chemical composition

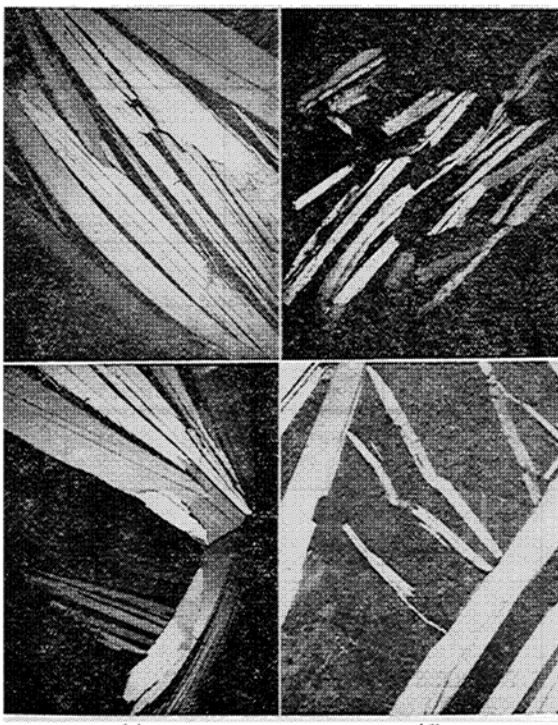


Fig. 6. Microphotograph of fluor-phlogopite (1).

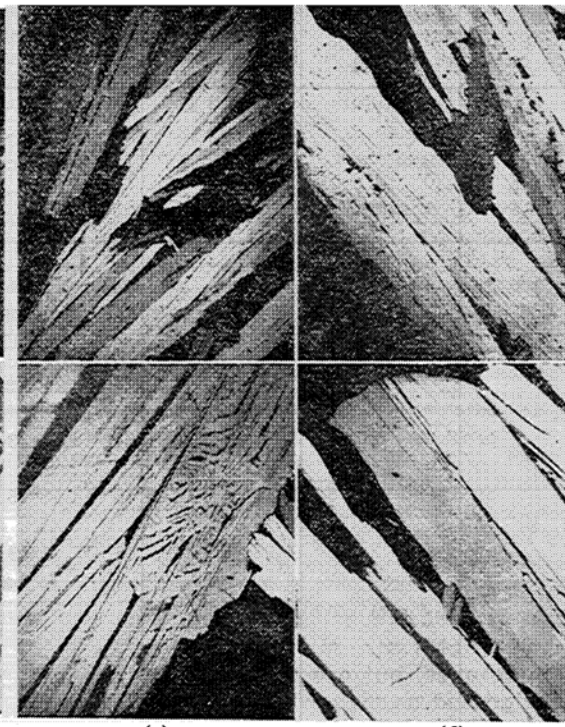


Fig. 7. Microphotograph of fluor-phlogopite (2).

of the product of experiment No. 13, given in Table IV, shows a remarkable increase of silica and alumina content, a slight increase of potassium and a slight decrease of fluorine. Because the excessive potassium of the batch usually concentrates in the glassy part of solidified mass, the analysed sample may have contained a slightly larger amount of glass than average. However, it seems to be essential that in order to obtain good large crystals, the fluorine and potassium content of the melt must not be deficient.

Microscopic Observation.—Curved crystals were often found in solidified masses. Some crystals bent 90° or more. A slightly curved crystal is shown in Fig. 6a. The curved crystals may have been bent by crystals growing from other directions. The curved crystals retain their form after they have been split from the mass. Sometimes the growing pressure of the other crystals was so great that the bent crystal was deformed to become a mosaic crystal, as shown in Fig. 6c. In Fig. 6b there is another example of imperfect curved crystals. Small crystals grown in interstices between large crystals perpendicular to the basal plane of large crystals were bent and ruptured by the pressure of contraction action on the basal planes of large crystals while the temperature was cooling (Fig. 6d).

As was previously described, large basal plates found in solidified masses often separated into small fragments. These plates were almost entirely composed of small crystals grown in the same direction or slightly inclined toward each other or were imperfect skeleton crystals, as shown in Fig. 7a, b, and c. All these crystals were formed by rapid cooling. With slow cooling, we obtained perfect crystals grown parallel to each other (Fig. 7d), which when split made clear single crystals.

Summary

Synthetic mica crystal growing experiments were carried out with a graphite crucible and a well-sintered high-aluminous clay crucible in a carbon granule resistance furnace of 30 kg. melting capacity, specially designed for this purpose. In experiments with a graphite crucible, the

melt often became supercooled and crystallized rapidly, to result in small crystals once crystallization started at the supercooled temperature. With a clay crucible, several experiments failed because of cracks in the crucible or because of corrosion of the crucible by the melt. Only with a well-sintered high-aluminous clay crucible and under the condition of small loss of fluorine and potassium in the melt were perfect large single crystals measuring about 5 cm. by 5 cm. formed even at a mean cooling rate of 2~5°C/hr. in the range of 1360°C to 1300°C. The yield of large single crystals was very small, doubtless because only the few crystals which had formed earlier had enough time and space to be in contact with the melt and thus to grow to large size. If the growing crystals come into contact or collide with other growing crystals, the crystals are either prevented from growing further or become strained or bent. Consequently, for crystals to grow to a large size, they must be in contact with the melt for a long time without being disturbed by other crystals. This can be done when crystals grow in the same direction. It was found that the temperature gradient of 4~5°C/cm. was necessary for crystals to grow in one direction.

Among many factors affecting the growth of crystals, the rate of cooling should be controlled to secure the rate of crystal growth at less than 0.06 mm./min. in order to grow perfect and flawless single crystals of mica.

Needless to say, a sufficient volume of melt is necessary to grow large crystals, i. e. a large quantity of melt gives more opportunity for large crystals to grow. Crystals measuring 5 cm. by 5 cm. were never obtained before the 30 kg. melting experiments were carried out.

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