Synthetic Mica Research*

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Introduction

Research in the production of synthetic mica was initiated in 1938 in response to the need of a local supply of high-grade mica. Experimental work was begun in January 1939 and directed originally to find compositions which crystallized easily. It was necessary to determine the temperatures of crystallization of mica in order to proceed with the work. The temperatures and velocities of crystallization were measured. Experiments to obtain large crystals were continued simultaneously with the above measurements. The corrosion of crucibles by the melt became more serious as the charge of melting increased and the rate of cooling decreased. Suitable crucibles for the synthetic work were investigated.

Temperatures of Crystallization and the Velocities of Crystallization of Synthetic Mica

The theoretical chemical formula of the fluorphlogopite is $KMg_3AlSi_3O_{10}F_2$ or 0.5 K_2O, 2.0 MgO, 1.0 MgF_2, 0.5 Al_2O_3, 3.0 SiO_2. If the ratio of MgO to MgF_2 in the folmula is varied, subsequent compositions can be represented by points in the three component system of phlogopite-orthoclase-magnesium fluoride.(1) By replacing the orthoclase with other silicates and the magnesium fluoride with other fluorides, various compositions are represented by points in three component systems.

Systems used in representing the various compositions are:

POM	phlogopite-orthoclase-magnesium fluoride(2)
P(K6S)M	phlogopite-(0.5K_2O, 3SiO_2)-magnesium fluoride 3)
P(KS)M	phlogopite-(K_2O, SiO_2)-magnesium fluoride 3)
POA	phlogopite-orthoclase-aluminium-fluoride(4)
PO(Ks)	phlogopite-orthoclase-potassium silicofluoride(4)

Table 1

Exptl. designation	Chemical composition, mol					Constitution			Temp. of crystn. °C.
	K_2O	MgO	Al_2O_3	SiO_2	MgF_2	Phlogopite	Orthoclase	MgF_2	
POM 1	0.50	2.00	0.50	3.00	1.00	1.0	—	—	1361
POM 2	0.51	1.88	0.50	3.00	1.13	0.790	0.051	0.159	1348
POM 3	0.50	1.58	0.50	3.00	1.42	0.488	0.129	0.383	1307
POM 4	0.50	2.06	0.50	3.00	0.94	0.797	0.051	0.152 (MgO)	1332
POM 5	0.50	2.00	0.50	3.00	2.03	0.48	—	0.52	1329
POM 6	0.50	1.75	0.50	3.00	1.70	0.48	0.07	0.45	1322
POM 7	0.50	1.30	0.50	3.00	1.00	0.48	0.36	0.26	1317
POM 8	0.50	0.96	0.50	3.00	0.48	0.48	0.52	—	1356
							0.5 K_2O, 0.3 SiO_2		
P(K6S)M 1	0.50	1.58	0.40	3.00	1.40	0.50	0.125	0.375	1323
							K_2O, SiO_2		
P(KS)M 1	0.69	1.85	0.46	3.00	1.60	0.50	0.125	0.375	1296
P(KS)M 2	0.53	1.98	0.48	3.00	1.19	0.80	0.05	0.15	1340
					AlF_3			AlF_3	
POA 1	0.50	3.00	0.17	3.00	0.69	1.00	—	—	1362
POA 2	0.50	2.40	0.23	3.00	1.13	0.50	0.125	0.375	1333
					K_2SiF_6			$\frac{1}{3}$ K_2SiF_6	
POKs 1	0.26	2.63	0.54	3.00	0.43	0.50	0.125	0.375	1309
PKs 1	0.19	3.37	0.56	3.00	0.75	0.50	—	0.50	1320
PKs 2	0.19	3.37	0.56	3.00	0.47	0.80	—	0.20	1355
					K_3AlF_6			$\frac{1}{3}$ K_3AlF_6	
POKa 1	0.10	2.40	0.25	3.00	0.47	0.50	0.125	0.375	1300
PKa 1	—	3.00	0.33	3.00	0.67	0.50	—	0.50	1315
PKa 2	—	3.00	0.33	3.00	0.42	0.80	—	0.20	1350

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[*] This paper is an abstract of the summary of the work published on *Kogyo Kagaku Zasshi* (*The Journal of the Society of Chemical Industry, Japan* or *The Journal of the Chemical Society of Japan, Industrial Chemistry Section*) from 1943 to 1948 and *Kogyo Butsuri Kagaku* (*Industrial Physical Chemistry*), 1948, No. 1, 108–119, and 1949, No. 2, 179–203.

(1) Tokiti Noda and Sachio Sugiyama, *Journ. Soc. Chem. Ind., Japan*, **46**, 921 (1943), *Suppl. Bind.*, 193 B (in English).

(2) T. Noda and S. Sugiyama, *ibid.*, **46**, 1082 (1943), *Suppl. Bind.*, 225 B; **47**, 320 (1944).

(3) T. Noda and S. Sugiyama, *ibid.*, **47**, 623 (1944).

(4) T. Noda and S. Sugiyama, *ibid.*, **47**, 625 (1944).

P(Ks)	phlogopite-potassium silicofluoride(5)
POKa	phlogopite-orthoclase-potassium aluminofluoride(6)
PKa	phlogopite-potassium aluminofluoride.(6)

The "quenching" method was used for the measurement. Raw materials used were chemically pure silicium oxide, magnesium oxide, aluminium oxide, magnesium oxide, potassium carbonate and fluorides. The mixture of a definite proportion of these raw materials was enclosed in a small platinum tube and suspended with a platimum wire in a platinum ribbon resistance furnace and heated to 1420°~1430°. After completely melted, the specimen was cooled to a desired temperature and maintained at the temperature for one hour or more and quenched. The experimental results are shown in Table 1. Temperature of crystallization means the temperature where mica crystals begin to appear.

In general, good results were obtained with compositions which contained large concentrations of phlogopite. In POM group, POM2 gave the best reusult. As the melt of orthoclase has a high viscosity and solidifies into hard glass, its presence in large amounts is not favorable. Melts of P(K6S)M and P(KS)M compositions gave softer and better splitting mica than POM composions. Better tesults were obtained with phlogopite-fluoride two-component compositions. Among various fluorides tested, potassium silicofluoride gave the best result and magnesium fluoride the next.

The velocity of crystallization of several compositions was measured by the same method as the measurement of the temperature of crystallization. Specimens maintained at a definite supercooled temperature for various periods were quenched. The velocity was calculated from the largest dimension of produced crystals. The results are shown in Table 2.

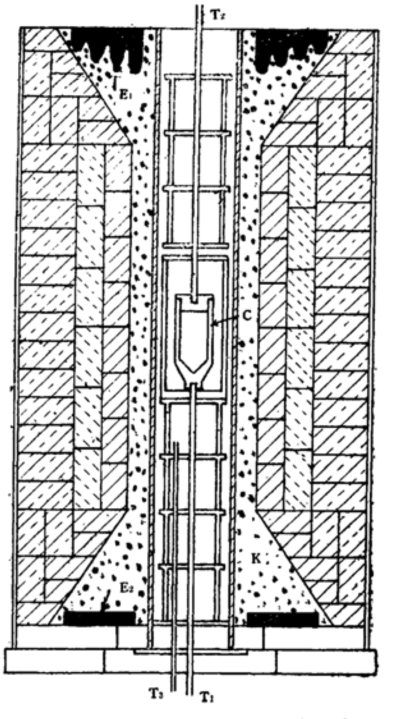
Table 2

Specimen	Temp. of crystn. °C.	Degree of supercolling °C.	Max. velocity of crystn. mm./min.	Approx. no. of nuclei, no./3 mm².
POM 3	1307	6	0.12	——
POM 2	1348	3	0.08	one to several
		6	0.16	10 to 30
		10	0.47	several tens
		20	0.40	many
P(KS)M 1	1296	3	0.13	——
P(KS)M 2	1340	3	0.10	4 to 8
		6	0.18	20 to 40
		10	0.59	many

The velocity of crystallization increases to a maximum point and then begins to decrease, as the degree of supercooling increases. The number of nuclei increases rapidly with the degree of supercooling. Therefore, it is desirable to maintain a minimum degree of supercooling with sacrifice of the velocity, in order to produce as large crystals as possible in a given space.

Experiments on the Formation of Large Crystals

A large number of the experiments were performed in a small scale with a platinum resistance furnace and in a somewhat larger scale with a cryptol resistance furnace of about 1kg. capacity. A large variety of compositions were tested, but the formation of large crystals resulted with the compositions in the neighborhood of POM 2. From PKs 2 easily splitting mica crystals were produced. Sometimes, calcined silica, alumina, and magnesia were mixed with potassium carbonate and heated to about 900° to drive off carbon dioxide. The heated mass was powdered and mixed with magnesium fluoride, pressed and filled in the crucible. In other cases, calcined oxides, potassium carbonate and magnesium fluoride were mixed and pressed without the preliminary heating. The filled crucible was covered with a lid and put in a larger grog crucible. The space between the two crucible was filled with granulated grog. The assembled crucible was set in the proper position of the furnace. A general section of the furnace is shown in the figure. The crucible was heated slowly to about 900° and from 900° to 1420~1450° as quickly as possible to avoid the loss of fluorine. When the charge in the crucible was melted completely, it was cooled to 1400°~1380° and from that temperature to 1300° slowly at the rate of 2~3° per hour. After passing this temperature



Vertical section of the cryptol resistance furnace: T_1,T_2,T_3, thermocouple; C, graphite crucible; E_1, E_2, iron electrode; K, cryptol.

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(5) S. Sugiyama, *Journ. Soc. Chem. Ind., Japan*, **48**, 14 (1945).

(6) S. Sugiyama, *ibid.*, **48**, 15 (1945).

range, the current was cut off. After the furnace was cooled down, the crucible was taken out. The temperature of the charge was measured by thermocouples continuously and by an optical pyrometer frequently.

Three methods were tested to start the crystallization from one point.

(a) The upper part of the melt was kept at higher temperature, so that nuclei would be formed at the cone-shaped bottom and grow upward. This method was used most frequently. It was somewhat difficult to control the temperature gradient as desired with the cryptol furnace.

(b) An inner graphite crucible, whose horizontal section was triangular or fan-shaped, was placed in the melting crucible. The inner crucible had a small hole at the corner of the bottom. When the melt was cooled, the part between the inner and the outer crucibles solidified first. The peeped crystal from the small hole of the inner bottom might have become a starting point for crystallization of the inner melt. Comparatively large crystals were formed in the small inner space.

(c) A platinum plate attached on a water-cooled brass pipe was dipped in the melt. Crystals attached rapidly on the plate. The plate was then raised very slowly, as a single crystal grew vertically downward.

Although the latter two methods were tried but not many times, they seemed to be promising.

Originally, high aluminous grog cruibles were used. With longer contact with the melt, these crucibles were attacked seriously. Various kinds of crucibles obtained in the market were tested. Sintered alumina crucible resisted very well, but it was not used because of its high cost. In a large number of experiments, artificial graphite crucibles were used. They can be used repeatedly, since the solidified mass separates easily from the crucible. But graphite makes a reducing atmosphere in the crucible and changes the composition of the melt more easily than neutral atmosphere. This reducting atmosphere colors the mica block gray, therefore it is desirable to operate in neutral or oxidizing atmosphere.

It was observed that aluminium oxide came from aluminous or grog crucible reacted with the melt and precipitated magnesium spinel. Spinel was very stable in the melt. Several compositions of the MgO-Al_2O_3-SiO_2 system were tested for corrosion. Specimens of spinel accompanying small amount of periclase and forsterite were very stable. Good sintered specimens of mullite or forsterite-periclase resisted sufficiently good, too.(7)(8)

Properties of Synthetic Mica

The chemical composition and the optical properties of synthetic mica are shown in Table 3.(9)

The synthetic mica is stable at high temperatures up to 1100° and begins to decompose at 1200° by liberating small amounts of gas.(10)(11) The liberated gas contained silicium tetrafluoride in large amounts.(11)

Preparation of Various Kinds of Mica by Isomorphous Substitution

Various kinds of mica were prepared by substituting the tetrahedral aluminum, octahedral magnesium and cubo-octahedral potassium of phlogopite by their crystal chemical equivalent elements.

A. Substitution of Tetrahedral Aluminium

(*a*). **Boron-phlogopite.**(12)—The mixture of 0.50 K_2O, 1.50 MgO, 1.50 MgF_2, 0.50 B_2O_3, 0.05 Al_2O_3, 3.00 SiO_2 melted clearly at 1250° and

Table 3

Specimen	Chemical composition						Optical properties					Chemical formula
							Refractive Index				Optical angle, 2 E	
	SiO_2 %	Al_2O_3 %	MgO %	K_2O %	F %	Total %	α	β	γ	γ-α		
1	42.01	16.84	26.61	8.66	5.70	99.81	1.522	1.553	1.554	0.029	19°	$(O_{0.7}F_{1.3})K_{0.8}Mg_{2.8}Al_{0.4}$ $(Al_{1.0}Si_{9.0}O_{10.0})$
2	40.73	18.50	25.41	9.20	6.03	99.87	1.544	1.564	1.566	0.029	20°	$(O_{0.6}F_{1.4})K_{0.8}Mg_{2.7}Al_{0.4}$ $(Al_{1.2}Si_{2.8}O_{10.0})$
3	43.44	13.90	26.95	9.68	6.16	100.12	1.513	1.539	1.540	0.027	22°	$(O_{0.6}F_{1.4})K_{0.9}Mg_{2.9}Al_{0.3}$ $(Al_{0.9}Si_{3.1}O_{10.0})$

Table 4

	Chemical composition						Chemical formula	Optical properties					Specific gravity
	SiO_2 %	B_2O_3 %	Al_2O_3 %	MgO %	MgF_2 %	K_2O %		α	β	γ	γ-α	2 E	
(1)	43.5	9.4	2.7	21.1	14.3	11.1	$(F_{1.80}O_{0.19})K_{0.9}Mg_{2.97}Al_{0.10}$ $(Al_{0.10}B_{1.07}Si_{2.86}O_{10.00})$	1.506	1.526	1.529	0.020	13°	2.730
(2)	43.4	9.8	1.5	19.8	15.2	11.2	$(F_{1.95}O_{0.05})K_{0.95}Mg_{2.94}Al_{0.10}$ $(B_{1.12}Si_{2.88}O_{10.00})$	1.505	1.521	1.522	0.017	27°	2.731
(2′)								1.501	1.526	1.518(calc.)			

(1) melted in grog crucible, (2) melted in platinum crucible, (2′) calculated(13)

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(7) T. Noda and Masao Konno, *Journ. Ceramic Soc., Japan*, **57**, 25 (1949).

(8) T. Noda and Kiyoshi Mori, *ibid.*, **57**, 104 (1949).

(9) T. Noda and S. Sugiyama, *Journ. Soc. Chem, Ind., Japan*, **46**, 760 (1943), Suppl. Bind., 162 B.

(10) T. Noda and Koichi Aoki, *ibid.*, **51**, 7 (1948).

(11) T. Noda and Torû Matsushita, *ibid.*, **51**, 83 (1948).

(12) T. Noda, Nobutoshi Daimon and Hitoshi Toyoda, *ibid.*, **47**, 449 (1944).

(13) T. Noda and Daimon, *Journ. Electrochem. Soc., Japan*, **14**, 125 (1946).

began to crystallize at 1150°. The chemical compositions and the optical properties of the produced mica crystals are as shown in Table 4.

(*b*). **Zinc-mica.**(14)—To the mixture of 0.50 K_2O, 1.50 MgO, 1.50 MgF_2, 0.50 ZnO, 0.05 Al_2O_3, 3.50 SiO_2 was added excess ZnO to cover the loss by evaporation. The mixture was melted in a grog crucible and cooled. Comparatively good mica crystals separated out. The chemical composition of the mica is:

SiO_2, 41.58%; ZnO, 7.03%; Al_2O_3, 9.06%,
MgO, 17.83%; MgF_2, 14.11%; K_2O, 10.75%.

The chemical formula is $F_{2\cdot0}K_{1\cdot0}Mg_{2\cdot9}Zn_{0\cdot2}(Zn_{0\cdot2}Al_{0\cdot8}Si_{3\cdot0}O_{10\cdot0})$.

(*c*). **Beryllium-mica.**(14)—The mixture of 0.50 K_2O, 1.90 MgO, 1.10 MgF_2, 0.50 BeO, 0.05 Al_2O_3, 3.00 SiO_2 melted at about 1350°. Mica crystals separated by cooling.

(*d*). **Iron-mica.**(14)—The mixture of 0.50 K_2O, 1.50 MgO, 1.50 MgF_2, 0.50 Fe_2O_3, 0.05 Al_2O_3, 3.00 SiO_2 crystallized out black to brown mica.

B. Substitution of Cubo-octahedral Potassium(15)

(*a*). **Natrium-mica.**—The mixture of 0.50 Na_2O, 1.50 MgO, 1.50 MgF_2, 0.50 Al_2O_3, 3.00 SiO_2 melted at about 1325°. Mica crystals obtained were small.

(*b*). **Calcium-mica.**—The mixture of 0.50 CaO, 1.50 MgO, 1.50 MgF_2, 0.50 Al_2O_3, 3.00 SiO_2 melted at about 1200°. Rapid cooling resulted glass. By slow cooling, minute mica crystals were obtained.

(*c*). **Strontium-mica.**—The mixture of 0.50 SrO, 1.50 MgO, 1.50 MgF_2, 0.50 Al_2O_3, 3.00 SiO_2 melted at about 1450°. Small mica crystals were obtained.

(*d*). **Barium-mica.**—The mixture of 0.50 BaO, 1.50 MgO, 1.50 MgF_2, 0.50 Al_2O_3, 3.00 SiO_2 melted at about 1400°. Mica crystals obtained were large, but brittle and difficultly splitting. The mixture of 1.00 BaO, 1.50 MgO, 1.50 MgF_2, 1.00 B_2O_3, 2.00 SiO_2 melted at about 1200°. By rapid cooling glass formed, by slow cooling, small mica crystals crystallized.

C. Substitution of Octahedral Magnesium and Preparation of Colored Mica(16)

The following mixtures shown in Table 5 produced mica crystals. (The temperature of melting by reaction and the colors of the produced mica crystals are also listed).

Table 5

Cemical composition of mixtute	Temp. of melting °C.	Color of mica
0.5 K_2SiF_6, 1.5 MgO, 1.5 MnO_2, 0.5 Al_2O_3, 2.5 SiO_2	1350	brown
0.5 K_2SiF_6, 1.5 MgO, 1.5 FeO, 0.5 Al_2O_3, 2.5 SiO_2	1350	brack
0.5 K_2SiF_6, 2.75 MgO, 0.25 $NiCO_3$, 0.5 Al_2O_3, 2.5 SiO_2	1400	yellowish green
0.5 K_2SiF_6, 2.75 MgO, 0.08 Co_3O_4, 0.5 Al_2O_3, 2.5 SiO_2	1400	pink -
0.5 K_2SiF_6, 2.75 MgO, 0.09 Cr_2O_3, 0.5 Al_2O_3, 2.5 SiO_2	1400	yellow
0.5 K_2SiF_6, 2.75 MgO, 0.125 NH_4VO_4, 0.5 Al_2O_3, 2.5 SiO_2	1400	
0.5K_2 SiF_6 2.0MgO, 1/3 Co_3 O_4, 0.5B_2O_3, 2.5SiO_2	1200	blue
0.5 K_2O, 2 LiF, TiO_2, 0.5 B_2O_3, 3 SiO_2	1100	faint pink
BaF_2, 2 MgO, 0.5 Li_2CO_3, 0.5 B_2O_3, 3 SiO_2	1100	white
SrF_2, 2 MgO, 0.5 Li_2CO_3, 0.5 B_2O_3, 3 SiO_2		white
CaF_2, 2 MgO, 0.5 Li_2CO_3, 0.5 B_2O_3, 3 SiO_2		white

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(14) T. Noda and N Daimon, *Journ. Soc. Chem. Ind., Japan*, **49**, 125 (1946).

(15) T. Noda, N. Daimon and Utai Songkram, *Journ. Ceram. Soc., Japan*, **52**, 95 (1944).

(16) N. Daimon, Not yet published.