

SYNTHETIC MICA

ITS PROPERTIES AND APPLICATION

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1. Historical Survey and Present Status

Mica is one of the most important electric insulators. Mica crystals of special quality are required for radio tube spacers and condenser dielectrics. Built-up mica is used in large quantities in electric machines, such as motors and generators.

However, because a few countries, such as India, Brazil and the United States, produce a greater part of the world's supply of good quality mica for electric uses, it was a quite reasonable sequence that Japan and Germany having no natural resources of good quality mica, contemplated the synthesis of mica for practical purposes.

The first synthetic mica crystals were found in blast furnace slags in 1822 in Sweden. Since that time in Germany, France and Russia a number of experiments were carried out, chiefly by mineralogists who were interested in the artificial formation of mica, a common rock-forming mineral. Because the experiments were carried out in the period from the 1880's to the 1920's, these reports described qualitative observations on the formation of mica and the role of fluorides was thought to be effective only as mineralizer.

Beginning in 1934, D. P. Grigoriev of Russia carried out the synthesis of mica and interpreted the results from the modern point of view. He obtained crystals of several millimeters in width and his published papers on synthetic mica attracted the author's attention.

The Science and Technical Council associated with the Government of Japan published in 1938 a report in which a shortage of good quality mica as a strategic material was described. This report so stimulated the author that he immediately began synthetic mica research. At about the same time, S. Nagai, Professor of Tokyo University, began experiments along the same line.

In 1941 there was organized a synthetic mica subdivision of the Seventeenth Special Committee of the Japanese Society for the Promotion of Science. This subdivision was presided over by Yuji Shibata, Dean of the Faculty of Science, Nagoya University.

All literature on synthetic mica up to that time was reviewed as completely as possible. Abstracts of all researches were arranged chronologically and published in the Journal of the Ceramic Association of Japan¹⁾ as a report of that Committee, and their research work was pursued actively.

Measurements of temperature of crystallization of fluor-phlogopite, its rate of crystallization, and the synthesis of several substituted micas were carried out along with the crystal growing experiments of synthetic mica.²⁾³⁾ As a result, in 1944

single crystals of 1 cm by 2 cm were prepared in 1 to 2 kg experiments.

It was hoped to carry out a large scale experiment in order to prepare large single crystals of mica, and the research group was rearranged as a Wartime Research Project headed by the author. However, even though the rearrangement was partially aimed at getting more easily the necessary material for constructing a large furnace, it was extremely difficult to obtain steel plates and other strategic materials at that time and the furnace could not be constructed during the War.

General descriptions of the synthetic mica research carried out in Germany during the War and of the progress in researches on the same project in Japan and in the United States after the War were included in the author's summaries.^{(1,7)†} Therefore only an outline of the present status of the manufacture of synthetic mica in Japan and in the United States will be given.

The Tokyo-Shibaura Electric Co. is the only manufacturer of synthetic mica in Japan. The Mazuda Laboratory of the company began their research in the pre-war period. Melting experiments using 100-pound glass melting crucible in a gas-fired furnace were carried out as a Wartime Research Project which was headed by the author, but the experiment failed because of the corrosion of the crucible. After the close of the War, a new staff took over the job of continuing the work and since 1952 has carried out a pilot plant experiment with the subsidy of the Ministry of International Trade and Industry. Their experiment was completed in 1955.⁽²⁶⁾

Calcined sea-water magnesia, alumina, quartzite powder, and potassium fluosilicate as raw materials were used. Batch of the composition approximately corresponding to fluor-phlogopite is heated in a crucible within a furnace for melting to a clear liquid. The melt which results is then cooled down slowly to crystallize the mica in the vicinity of its crystallizing temperature range 1,400°-1,350° C. In spite of the corrosiveness of the fluor-phlogopite melt, Tokyo-Shibaura people found that well-sintered high aluminous clay crucible was sufficiently resistive to the corrosion of the melt to be used in a slow-cooling procedure of crystallization on a commercial scale.

When the crystallized mass is cooled, it is taken out by breaking the crucible and broken into several blocks. Sizes of produced crystals depend on the batch composition, procedure of melting, rate of cooling, and on other factors. Single crystals measuring up to 6 cm by 5 cm, with a thickness of 0.8 mm were produced in the Mazuda Laboratory. Fig. 1 shows single crystals of synthetic mica.

Single crystals larger than 2 cm by 2 cm can be used for making radio tube spacer. However, percentage yield of these single crystals is still small. Therefore, the prevailing need for development of synthetic mica production is a further research for commercial uses of small mica crystals, as the highest limit of economical production of synthetic mica depends on the size of the demand for small crystals.

In the United States, the Owens-Corning Fiberglas Corporation with the Corning Glass Works was the first to be interested in the research of synthetic mica and began work in 1945 based on that done in Germany. Afterwards, the synthetic mica research project was centered in the Electrotechnical Laboratory (ETL), Bureau of Mines, where experiments were carried out successfully on a large scale

† Also refer to Rustum Roy,⁽¹⁸⁾

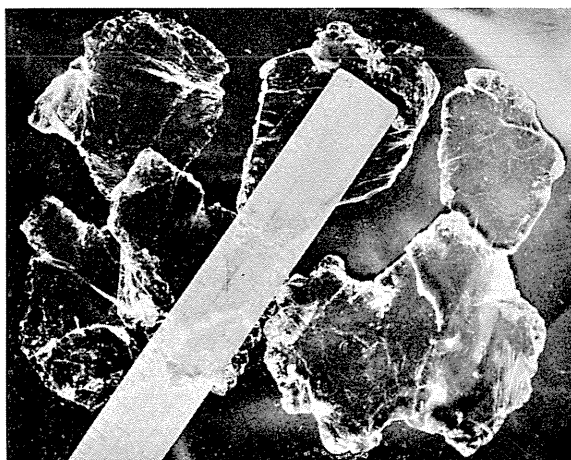


FIG. 1. Single crystals of synthetic mica. (Courtesy of Tokyo-Shibaura Electric Co.)

to develop it to an industrial production. They used crucible as a container of melt in an earlier stage of the research. However, since 1951 they developed an internal heating electric melting method for the production of synthetic mica and carried out a melting of 8 tons in 1953. The Synthetic Mica Corporation, a subsidiary of the Mycalex Corporation of America, completed their 1,000 ton a year plant and began the production in August, 1955.⁵⁾

This method⁶⁾ is composed of passing the electric current through a graphite resistance rod which connects two graphite electrodes embedded in the synthetic mica batch, and resulting in a melt inside the batch. As the mass of the melt increases, two graphite electrodes are connected electrically with the melt. Therefore, the further melting of the batch can be made by passing the electric current through the melt, even after the burn-out of the graphite resistance rod.

This melt is surrounded by the original batch and a dome is formed above the melt within the batch. Therefore, there is no corrosion problem of the container and the change of the composition of the melt by the vaporization of fluoride is small.

Power consumption per unit weight of the product is about 1 KWH/kg in about a 6 ton melting. Although a melting of several tons of batch in a single run can be carried out easily, large single crystals are not necessarily produced even with a large scale melting by this method. While single crystals of 8-9 cm in size were obtained, the percentage yield of large crystals seemed to be small and most of the crystals obtained were of thumb-nail size. Several conceivable reasons for this small percentage yield of large crystals are given in the author's summary.⁷⁾

2. Properties of Crystals

Crystal Structure and State of Crystal Deposit.

a. Crystal Structure

It seems to be unnecessary to describe the crystal structure of mica because

many textbooks on crystal chemistry and mineralogy contain full description of the structure. Therefore, only a scheme of crystal structure of mica is given in Fig. 2 as a convenience of reference for the following description.

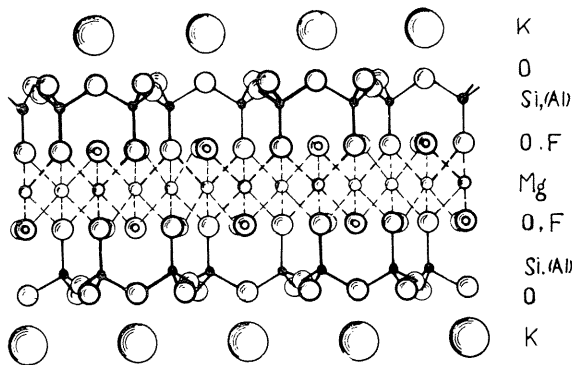


FIG. 2. Scheme of crystal structure of mica.

As is well known, silicon ion is surrounded tetrahedrally by four oxygen ions; magnesium ion octahedrally by five oxygen ions and a hydroxyl ion; potassium ion by twelve oxygen ions.

Lattice constants of fluor-phlogopite were determined accurately by Cohn and Hatch.⁸⁾ There are several possibilities of mode of overlapping of so-called mica layer ($\text{Mg}_6\text{Al}_3\text{Si}_6\text{O}_{20}\text{F}_4$) which may cause the occurrence of polymorphism of mica crystal.

b. State of Crystalline Deposit

It was found that mica crystals grow larger in a melt containing a slight excess over 100% of theoretical amounts of fluoride and silicate than in a melt of 100% mica composition.⁹⁾ Even when the melt is prepared from a batch of 100% mica composition, the composition of the melt deviates from the original batch because of both evaporation of fluorine and dissolution of container material at higher temperatures. Fluorine evaporates in forms of silicon fluoride, potassium fluoride and/or hydrogen fluoride. Therefore, mica usually crystallizes in a highly concentrated solution of fluor-mica.

The mica crystal structure has strong chemical bonds along its cleavage plane. The crystal grows faster along this plane than any other plane. The rate of growth along this plane is of the order of 1 to 0.1 mm per minute and is affected by the composition of melt and the degree of supercooling of melt.^{2) 3)} The rate of growth perpendicular to this plane, i.e. along *c*-axis seems to be much smaller. Thus very thin sheets of mica crystal are likely to separate in the melt with thin films of residual melt between sheets. As a result, there exist thin films of glassy substances between mica crystal sheets, and there are often thin films of glassy substance between cleavage planes even in clear single crystals of fluor-phlogopite. Also natural mica crystals often have thin films of foreign minerals between cleavage planes. Properties of mica crystals are affected by the amount and quality of these inclusions. In most cases glassy substance and fluorides were observed as inclusions of synthetic mica. In a few cases fluor-humite was found.¹⁰⁾

3. Physical and Chemical Properties

Measurements of electrical and optical properties, tests on mechanical properties and vacuum characteristics, investigations on thermal stability and hydrothermal reaction with aqueous solutions all were carried out chiefly with single crystals or with powder crystals, in some cases with hot-pressed mica products. Results of these investigations published heretofore are here summarized.

a. Electrical Properties

Data on fluor-phlogopite are comparatively scanty and are shown in Table 1. Data on natural phlogopite and muscovits are shown together for convenience of comparison. It is probable that further measurements will improve values of power factor of fluor-phlogopite. Power factor of hot-pressed fluor-phlogopite ceramics measured by Comeforo, Hatch and Eitel¹¹⁾ was 2×10^{-4} (1 MC). Electrical properties of fluor-phlogopite seem to be superior to natural phlogopite and they may be the same as those of natural muscovite of good quality.

TABLE 1. Electrical Properties of Synthetic and Natural Micas

	Synthetic fluor-phlogopite*	Natural phlogopite*	Synthetic fluor-phlogopite**	Natural muscovite**
Volume resistivity	8×10^{15}	10^{10} - 10^{14}	—	—
Dielectric constant	6.2(5-10 MC)	5- 6(5-10 MC)	6.3(1 MC)	5.4(1 MC)
Power factor (10^{-4})	18 (5-10 MC)	30-70(5-10 MC)	2 (1 MC)	3 (1 MC)
Dielectric strength (kg/mm)		25-70	87	110

* Values from T. Ishikawa, *Material (Japan)*, **3**, 11-14 (1955).

** Values from R. A. Humphrey, *Mycalex Corp. America, Information Pamphlet* (1954).

Daimon and Matsushita¹²⁾ measured dielectric constants and power factors of various types of substituted fluor-mica. Samples used for the measurement were prepared as follows: splitting the synthetic mica crystals from crystallized mass; powdering in a wet state; purifying by elutriation and being separated by using heavy liquid. Purified mica powder thus obtained was mixed with paraffin and pressed to form a disk specimen for measuring dielectric constants and power factors. The values of mica crystals were calculated from the measured values of dielectric constant E and power factor κ of the mixture and of dielectric constant E_p and power factor κ_p of paraffin wax using the following equations:

$$\ln E_m(\ln E - X_p \ln E_p) / X_m^{13)} \quad \text{and} \quad \ln \kappa_m = (\ln \kappa - X_p \ln \kappa_p) / X_m.^{14)}$$

where X_p and X_m are volume fractions of paraffin wax and mica crystals, respectively in the mixture.

The value of the dielectric constant of normal fluor-phlogopite is 6.1 at 1 MC. This value does not change greatly when tetrahedral aluminum is replaced by beryllium, zink, boron, ferric iron, cobalt, and the like or in partial replacement of octahedral magnesium by its crystalchemical equivalent ion. However, remarkable changes in the values of dielectric constants and power factors can be seen when replacing potassium of twelve coordination position with its equivalent ion. The value of the dielectric constant of mica increases roughly twofold in replacing

TABLE 2. Chemical Composition and Electrical Properties of Various Types of Synthetic Mica*

Type of mica	Chemical composition**	Dielectric constant	Power factor
Normal F-phlogopite	$\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}\text{F}_2$	6.1	0.002
B-mica	$\text{KMg}_3(\text{Al}_{0.4}\text{B}_{0.6}\text{Si}_3)\text{O}_{10}\text{F}_2$	6.1	0.009
Be-mica	$\text{KMg}_3(\text{Be}_{0.5}\text{Si}_{3.5})\text{O}_{10}\text{F}_2$	6.7	0.002
Zn-mica	$\text{KMg}_3(\text{Zn}_{0.4}\text{Al}_{0.2}\text{Si}_{3.4})\text{O}_{10}\text{F}_2$	6.2	0.007
Fe^{3+} -mica	$\text{KMg}_3(\text{Fe}^{\text{III}}_{0.6}\text{Al}_{0.4}\text{Si}_3)\text{O}_{10}\text{F}_2$	6.4	0.002
Co^{6+} -mica	$\text{KMg}_3(\text{Co}_{0.3}\text{Al}_{0.2}\text{B}_{0.2}\text{Si}_{3.3})\text{O}_{10}\text{F}_2$	6.2	0.001
BaLi-mica	$\text{BaLiMg}_2(\text{Al}_{0.75}\text{B}_{0.25}\text{Si}_3)\text{O}_{10}\text{F}_2$	8.0	0.002
SrLi-mica	$\text{SrLiMg}_2(\text{Al}_{0.75}\text{B}_{0.25}\text{Si}_3)\text{O}_{10}\text{F}_2$	8.7	0.03
CaLi-mica	$\text{CaLiMg}_2(\text{Al}_{0.75}\text{B}_{0.25}\text{Si}_3)\text{O}_{10}\text{F}_2$	9.5	0.1
Fe^{2+} -mica	$\text{KMg}_{2.5}\text{Fe}^{\text{II}}_{0.5}(\text{AlSi}_3)\text{O}_{10}\text{F}_2$	6.1	0.002
Co^{2+} -mica	$\text{KMg}_{2.5}\text{Co}_{0.1}(\text{AlSi}_3)\text{O}_{10}\text{F}_2\text{K}$	6.3	0.05
Ni^{2+} -mica	$\text{KMg}_{2.5}\text{Ni}_{0.2}(\text{AlSi}_3)\text{O}_{10}\text{F}_2$	6.1	0.002
Mn^{2+} -mica	$\text{KMg}_{2.6}\text{Mn}_{0.4}(\text{AlSi}_3)\text{O}_{10}\text{F}_2$	6.5	0.004
Na-mica	$\text{NaMg}_3(\text{AlSi}_3)\text{O}_{10}\text{F}_2$	15.0	0.6
$\text{Ba}_{0.5}$ -mica	$\text{Ba}_{0.5}\text{Mg}_3(\text{AlSi}_3)\text{O}_{10}\text{F}_2$	7.1	0.007

* Values from N. Daimon and T. Matsushita, "Electrical Properties of Various Kinds of Synthetic Mica," J. Chem. Soc. Japan (Ind. Chem. Sect.), 55, 760-761 (1952).

** Compositions were rounded off, Values from N. Daimon, "Synthetic Research on Various Kinds of Mica," Memoir of the Faculty of Engineering, Nagoya University (in English), 5, (1), 126-130 (1953); J. Chem. Soc. Japan (Ind. Chem. Sect.), 55, 636-698 (1952); cf. T. Noda, "Synthetic Mica Research in Japan," J. Am. Ceram. Soc., 38, 147-152 (1955).

sodium for potassium. It can be seen from Table 2 that values of the dielectric constant increase as there is a decrease in ion size of twelve coordination position of group BaLi-, SrLi-, and CaLi- mica, and that values of power factors of micas increase as the ion size of twelve coordination position of mica decreases.

Data on electric properties of hot-pressed mica measured at the ETL are given in Table 3.¹¹⁾ These values are apt to be effected by the porosity of the product.

TABLE 3. Electrical Properties of Hot-Pressed Synthetic Mica*

Composition	Water absorption (%)	Bulk density (g/cc)	Power factor	Dielectric constant
Boron mica ($\text{KMg}_3\text{BSi}_3\text{O}_{10}\text{F}_2$)	2.0	2.70	0.0022	5.81
	0.8	2.71	0.0011	5.97
	0.4	2.75	0.0007	5.93
Normal F-phlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$)	<0.5	2.80	0.0010	6.30
Barium mica No. 1 ($\text{Ba}_{1/2}\text{Mg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$)	1.0	2.86	0.0008	5.87
Barium mica No. 2 ($\text{BaMg}_3\text{Al}_2\text{Si}_3\text{O}_{10}\text{F}_2$)	3.17	3.26	0.0008	7.20
	<0.1	3.51	0.0003	7.60
Barium mica No. 3 ($\text{BaMg}_{2.1/2}\text{AlSi}_3\text{O}_{10}\text{F}_2$)	<0.1	3.39	0.0009	7.55
Barium mica No. 4 ($\text{BaMg}_2\text{LiAlSi}_3\text{O}_{10}\text{F}_2$)	0.1	3.32	0.0004	7.88
Barium mica No. 5 ($\text{BaMg}_3\text{BeSi}_3\text{O}_{10}\text{F}_2$)	4.60	3.00	0.0005	7.70

* Values from J. E. Comeforo, R. A. Hatch, R. A. Humphrey and Wilhelm Eitel, "Synthetic Mica Investigations: I, A. Hot-Pressed Machinable Ceramic Dielectric," J. Am. Ceram. Soc., 36, 286-294 (1953),

That dielectric constants of barium containing micas are slightly larger than the constant of normal fluor-phlogopite and further that the replacement of tetrahedral aluminum with boron does not effect the dielectric constant remarkably, are results qualitatively coincident with Daimon's results.

b. Optical Properties

Mica crystal has a large birefringence which is a characteristic feature of layer lattice. Refractive index of silicate such as mica depends chiefly on the polarizability of anion, i.e. oxygen ion, and is only slightly affected by the replacement of cation in the crystal. As is well known, molecular refractivity of glass or of isotropic crystal can be calculated simply by adding products of the ionic refractivity and molar fraction of the component ion. However, in an unisotropic crystal, refractive index varies with the crystallographic direction of the crystal. For this reason Noda and Daimon¹⁵⁾ calculated refractive indices along *a*-, *b*-, and *c*-axis of mica using Bragg's method of calculation. It was assumed that oxygen ions in (SiO₄) tetrahedron are the chief contributors to the birefringence and that other constituent ions, if not all, only slightly affect the birefringence.

Chemical formulae and observed and calculated values of refractive indices of various kinds of substituted micas are shown in Table 4.^{15) 16)}

TABLE 4. Refractive Indices of Synthetic Mica*

Type of mica	Measured values			Calculated values				Specific gravity
	α	β	γ	α	β	γ	$\frac{\beta+r}{3}$	
B-mica.....	1.505	1.521	1.522	1.501	1.526	1.518	1.522	2.734
Be-mica.....	1.501		1.516	1.497	1.516	1.511	1.513	2.770
Zn-mica.....	1.524		1.553	1.534	1.557	1.550	1.554	2.965
BaLi-mica.....	1.549		1.587	1.563	1.585	1.580	1.583	3.338
SrLi-mica.....	1.527		1.556	1.542	1.566	1.558	1.562	3.129
CaLi-mica.....	1.519		1.547	1.532	1.555	1.549	1.552	2.789
Co ^p -mica.....	1.519		1.547	1.535	1.558	1.549	1.544	2.863
Ni-mica.....	1.514		1.539	1.524	1.547	1.540	1.544	2.841
Mn-mica.....	1.514		1.545	1.533	1.556	1.549	1.552	2.917
Na-mica.....	1.510		1.533	1.515	1.537	1.531	1.534	2.742
Ba _{0.5} -mica.....	1.517		1.546	1.522	1.547	1.538	1.546	2.986
Normal F-phlogopite...	1.544		1.564 ~1.566	1.540	1.567	1.556	1.562	2.852

* Values from (a) T. Noda and N. Daimon, "Calculation of Refractive Index and Birefringence of Mica," J. Electrochem. Assoc. Japan, **14**, 124-29 (1946) and (b) N. Daimon, "Refractive Indices of Various Synthetic Micas," J. Ceram. Assoc. Japan, **61**, 203-206 (1953).

Calculated values of α and $\frac{1}{2}(\beta+r)$ of most mica samples are in fairly good agreement with the observed values.

Natural muscovite shows an intensive absorption at 2.75 μ which is ascribed to hydroxyl. However, synthetic fluor-phlogopite shows no absorption at this point and also no absorption was observed up to 8.8 μ in the infra-red region. An intensive absorption band ranging from 8.8 μ to 10.8 μ and having a peak at 9.8 μ and corresponding to Si-O and Al-O bonds, was observed in addition to weak absorptions at 12.4 and 13.3 μ .¹⁷⁾

It was reported that small notches at 2.66 and 2.90 μ (West¹⁸⁾) and strong

absorptions at 5.4, 5.8, 6.1, 7.5, 13 and 13.5 μ and a 100% absorption between 9 and 11.2 μ (Sutherland¹⁸⁾) were observed.

Normal fluor-phlogopite shows on absorption in the visible region, while substituted fluor-micas containing transition elements show characteristic absorptions of these elements. Extinction coefficient curves of several substituted micas are shown in Fig. 3. Co^b -mica, in which cobalt occupies tetrahedral position, is blue in color, whereas Co^o -mica, in which cobalt has the octahedral coordination, is pink. Ni-mica is greenish yellow, Mn-mica is dark purple-brown, Fe^{III} -mica is brown, and Fe^{II} -mica is silver gray. Because of its low iron content, synthetic fluor-phlogopite is more transparent in ultra violet region than natural mica.¹⁹⁾

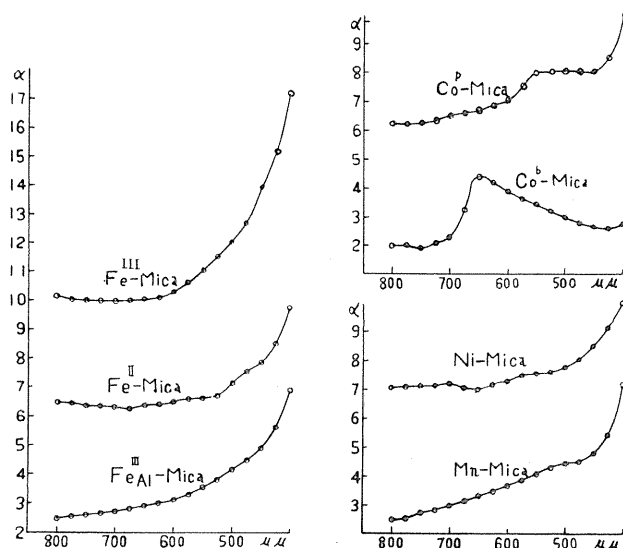


FIG. 3. Extinction coefficient curve of synthetic mica (Daimon).

c. High Temperature Stability and Vacuum Characteristics

The most characteristic feature of synthetic fluor-phlogopite is its superior high temperature stability, which is high compared with natural hydroxyl mica. Natural muscovite decomposes at about 600° C and liberates water. Natural hydroxyl-phlogopite liberates water at temperatures higher than muscovite, and its decomposition finishes at about 800° C. Yoder and Eugster²⁰⁾ investigated the stable region of hydroxyl-muscovite and of hydroxyl-phlogopite using high pressure bombs at elevated temperatures. According to his measurements, the equilibrium vapor pressure of hydroxyl-phlogopite is less than 70 kg/cm² at 800° C.

It was found^{21), 22)} that synthetic fluor-phlogopite showed almost no decomposition up to 900° C, only slightly decomposed at 1,000° C and that the rate of decomposition increased rapidly above 1,100° C, thus becoming remarkable at 1,300° C, when powdered specimen was heated in a dry air stream. The decomposition gas product consisted chiefly of SiF_4 . At higher temperatures KF was dominant in the decomposition gas product.²³⁾ The decomposition of fluor-phlogopite was accelerated with

a wet air stream and in that case besides the above mentioned fluorides, HF was liberated.

As the decomposition takes place from outside surface, the rate of decomposition may be less remarkable in large mica crystals than in powdered crystals. Therefore large crystals of fluor-phlogopite may be used without remarkable decomposition at higher temperatures than may be expected from the above experiment.

It was found that synthetic fluor-phlogopite liberated almost no gas when heated up to 800° C and only little gas at 900° C at a pressure of 10^{-5} mmHg. The total amount of gas liberated from room temperature up to 1,000° C was $2-3 \times 10^{-3}$ cc per gram of sample. This amount is the same as or even less than that from steatite product which was tested under the same condition. The amount of gas liberated between room temperature and 800° C was only 0.1×10^{-3} cc per gram of sample.²⁴⁾

According to Th. E. Hanley,²⁵⁾ synthetic normal fluor-phlogopite, after a 12-hour bake at 390° C, was placed in an Alpert-type vacuum system and the system pumped to a pressure of 2.2×10^{-9} mmHg. The mica sample lost about 0.8 mg per gram during the evacuation. Without the sample, the system reached 2.1×10^{-9} mmHg. A well degassed sample of nickel of equivalent volume gave about the same pressure when processed in the same manner as the mica. When 8.75 cc of sample of mica was air-baked at 800° C for one hour and sealed in a well-evacuated bulb, the pressure increased from 5×10^{-7} mmHg to 6×10^{-7} mmHg in 1,000 hours. The loss of the mica by heating in air was 11.7 mg per gram during the first 1½ hours, and was only 1 mg per gram during the following 20 hours.

This shows that it is preferable to air-bake the mica beforehand for use in vacuum tubes. Immersing the sample in boiling water for 1½ hours had little effect. It was proved that electron bombardment did not cause a liberation of fluorine from the mica.²⁶⁾

The use of synthetic fluor-phlogopite instead of natural mica may prolong the life of radio tubes. More important, is the expectation that the use of synthetic mica may make it possible to improve the design of radio tubes. It was proved by tests that the life of a miniature tube of the small power type, was the same whether synthetic mica spacers or natural mica spacers were used; but that the life of a miniature tube of a large power type, in which synthetic mica spacers were used, was longer than that of tubes in which natural mica spacers were used.²⁶⁾

d. Mechanical Properties

Although there are no quantitative data on mechanical properties of synthetic mica crystal, the mica is said to be harder than natural mica. It is not known whether this hardness is its own property or only an apparant one caused by glassy material which exists between cleavage planes of mica crystals.

The most characteristic feature of mica is its great cleavage along the basal plane. This cleavage results in thin flexible film crystals of mica which can be punched with tools. Synthetic mica crystals showed a clear punch without cracking. Punched holes in this mica were cleaner than those in natural mica when they were punched with the same machine by the same skilled worker. Spacers made of synthetic mica and a sample miniature tube are shown in Fig. 4.

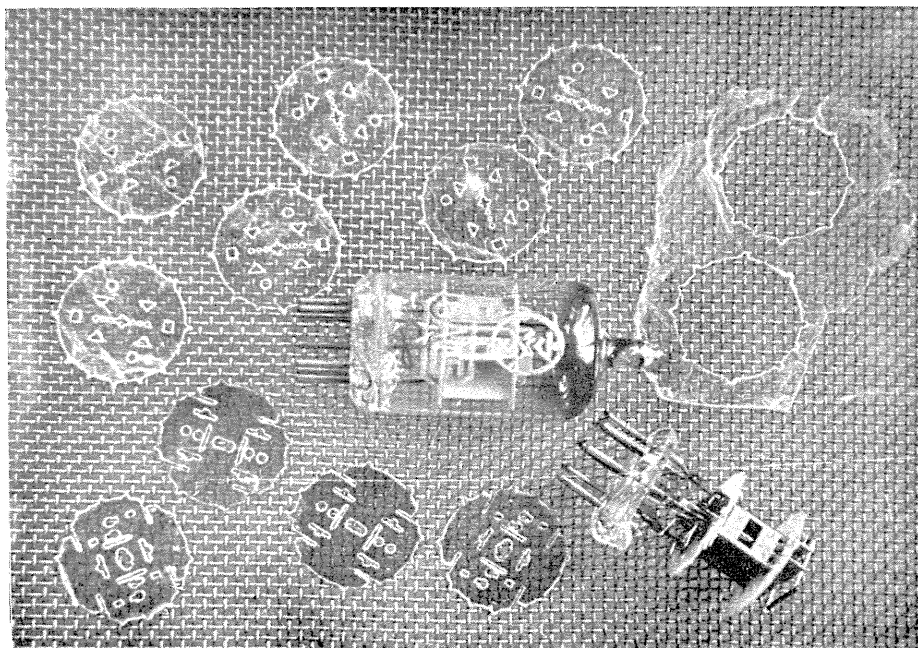


FIG. 4. Radio tube spacers made of synthetic mica, electrodes and a miniature tube using synthetic mica spacers. Lower-left spacers are made of natural mica. (Courtesy Mazuda Laboratory of Tokyo-Shibaura Electric Co.)

e. Hydrothermal Treatment of Blocks of Synthetic Mica Aggregates²⁷⁾ and Hydrothermal Reaction of Synthetic Mica²⁸⁾

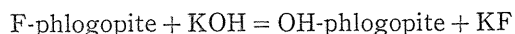
As above described, synthetic mica crystals are bonded so tightly together by a thin film of glass that it is frequently difficult to split crystals from crystallized block and sometimes a forced splitting causes damage to single crystals of mica. A crystal of synthetic mica itself has thin films of glass between its cleavage faces.

When blocks of aggregated mica crystals are treated hydrothermally with alkali, acid, or salt solution at elevated temperatures, glass between crystals and cleavage faces is corroded or it devitrifies and is easily separated from crystals. It results in an easy splitting of mica crystals and an increase of flexibility in mica crystal. Dilute alkalis, acids and salt solutions such as K_2CO_3 , $KHSO_4$, KF and the like were found to be effective as reagents for the treatment. In general, the higher the temperature of treatment and the larger the concentration of solution, the better was the effect for accelerating splitting. A treatment of synthetic mica blocks with a KOH solution of the concentration from $1/2 N$ to $1 N$ at temperatures ranging from 200° to $350^\circ C$ was sufficient to achieve a good accelerating effect for splitting. The effective time of treatment depends on the size of the blocks, at $200^\circ C$ a 24 hour treatment was sufficient for about a one kilogram block.

Blocks of aggregates of larger mica crystals could be treated effectively in a shorter period than blocks of smaller crystals, as the reacting solution could penetrate deeper into the mass along crystal sheets of the larger more easily than the smaller.

The fluorine content of the specimens was found to have been decreased by the hydrothermal treatment with alkali solutions. Temperature-weight loss curves of treated specimens suggested formations of small amounts of a certain hydroxide and the hydroxyl-mica.

In order to learn the effect of hydrothermal treatment on mica crystal itself, powdered fluor-phlogopite crystals were treated with $1/2 N$ or $2 N$ KOH solution at temperatures from 200° to 450° C under pressure for periods of from one to four weeks. The powdered sample was prepared by pulverizing split mica crystals to a size less than 2μ in a blender. The hydrothermally treated specimens were investigated by the X-ray diffraction method and the infra-red spectroscopic method. It was found that a part of fluor-phlogopite reacted in the solution to produce a new crystal phase. The new crystal phase had the same X-ray diffraction pattern as that of the original mica, except that the new crystal had a slightly larger (001) spacing than that of the original mica. This increase of (001) spacing was found to correspond with the difference between (001) spacings of hydroxyl- and fluor-phlogopite.²⁰⁾ Therefore, the interpretation of the formation of the new crystal phase is that there was the following reaction ;



and not that some OH ion entered the fluor-phlogopite lattice. If the reaction takes place according to the above equation, the formation of hydroxyl-phlogopite may be depressed to a minimum by adding KF to the reacting solution. In fact, it was proved that the formation of hydroxyl-phlogopite was greatly depressed when the synthetic mica blocks were treated with alkali solutions containing fluoride or with fluoride solution.

4. Mica Ceramics

a. Glass-bonded Mica

Large amounts of scrap mica, the result of the mining and production of sheet and block mica, accumulated for a long time in India without use. Shortly after World War I, P. B. Crossley endeavored to find some use for this scrap mica and after many experiments he finally was able to make an inorganic electric insulator out of mica powder and glass powder. This insulator, a glass-bonded mica, was formed by pressing the mixture of mica powder and glass powder under high pressures at several hundred degree Centigrade. Glass-bonded mica can be easily machined or molded to exact size. It was marketed first in England.

As described above, natural mica decomposes and liberates water when heated to high temperatures. Therefore, only a glass of low softening temperature, such as lead borate, can be used as a binder. Glass of low softening temperature usually has a low resistance to weathering and decreases its surface electric resistance when exposed in a wet atmosphere. However, it is possible to use a glass of higher resistance to weathering and with better electric properties as a binder of synthetic mica because synthetic mica can be heated up to about $1,110^{\circ}$ C with practically no change.

Following is the method of manufacture of glass-bonded synthetic mica²⁶⁾: Synthetic mica blocks are crushed by a crusher and pulverized in a stamp-mill and

TABLE 5. Properties of Glass-Bonded Mica Products

		Glass-bonded synthetic mica*	Glass-bonded natural mica*	Steatite*	Mycalex** 410	Mycalex* 400
Raw materials		Synthetic mica, glass	Natural mica, lead borate glass	Talc	Natural mica, glass	Natural mica, glass
Color		White	Silver gray	White		
Specific gravity (g/cc)		2.87	3-3.5	2.6-2.8	3.8	3.0
Hardness (Mohs)		3-4	3-4	7-8	150 (Brinell)	70 (Brinell)
Water absorption (%)		0	0	0	0	0
Specific heat (cal/g.°C)		—	0.2	0.19-0.22	0.14	0.17
Coefficient of linear expansion (30-300°C) (10 ⁻⁶ /°C)	⊥	7.48	7-8	7-9	11	10.2
	∥	11.8		—		
Thermal conductivity (cal/cm.sec.°C) 20-100°C	∥	—	0.00054	0.00054	0.0011	0.0012
Softening temperature (under load) (°C)		700	405	1,400	—	—
Tensile strength (kg/cm ²)		400-500	420	640	420	420
Compressive strength (kg/cm ²)	⊥	2,600	—	3,600	1,750	2,460
	∥	2,900	2,460			
Flexural strength (kg/cm ²)	⊥	1,400	—	1,400-1,600	920	1,050
	∥	1,200	1,200			
Cleaving force (kg)		400	380	—		
Impact strength (kg.cm/cm ²)	⊥	6-7	6-7	5-7	0.7 (ft. lb/in of notch)	1.85
	∥	6-7	6-7			
Volume resistivity (room temperature) (ohm-cm)		>10 ¹⁴	>10 ¹⁴	>10 ¹⁴	10 ¹⁵	2 × 10 ¹⁵
Surface resistivity (room temperature) (ohm)	72% r.H.	>10 ¹²	>10 ¹²	10 ¹⁰⁻¹²	—	—
	82% r.H.	>10 ¹¹	>10 ¹¹	—	—	—
After boiling for 2 hours		10 ¹¹	10 ¹¹	—	—	—
Dielectric constant (room temperature)		6.5-6.7 (5 MC)	8-9.5 (5 MC)	5.5-6.5 (5 MC)	9.2 (1 MC)	7.4 (1 MC)
Power factor (room temperature) (10 ⁻⁴)		17-20 (5 MC)	20-50 (5 MC)	10-20 (5 MC)	15 (1 MC)	18 (1 MC)
Dielectric strength (50 room temperature) (KV/mm)		15	15	20-30	16	20

* Values from Tokyo-Shibaura Electric Company, "Manufacture of Synthetic Mica for Vacuum Tube," Final Report, 1955, Ministry of International Trade and Industry, Oder No. 27.

** Values from Engineering Handbook and Catalog, Mycalex Corporation of America, 1952.

in a ball-mill, successively. Glassy substances and other inclusions in synthetic mica blocks are pulverized easier than mica crystal itself, so that the glassy substance and other inclusions can be separated from mica crystal by washing the crystals with water on a sieve.

The purified crystal powder is mixed thoroughly with a binder glass in a definite proportion. The mixture is pressed at room temperature, dried completely, heated up to about 1,000° C and pressed quickly into a mold by a high-speed oil-press. The temperature of the mold is kept at 200°–300° C or at highest, 400° C. The molded product is removed from the mold and then annealed in a furnace.

Properties of glass-bonded synthetic mica products are shown with those of natural mica products and steatite in Table 5.

Properties of glass-bonded mica products are affected by the raw materials, i.e., types of mica and binder glass, mixing ratios of the raw materials, method of processing etc.

Synthetic mica products have lower density, a higher softening temperature and a smaller power factor than natural mica products, other properties of synthetic mica products being almost the same as those of natural mica products. The difference between the properties of these two products depends chiefly upon the differences between the properties of the binder glass.

Glass-bonded synthetic mica products can be made to exact size and also formed into a flat plate without and curvature. The product is now applied as a base plate of a power tube, a frame of coil etc. Glass-bonded synthetic mica products are shown in Fig. 5.

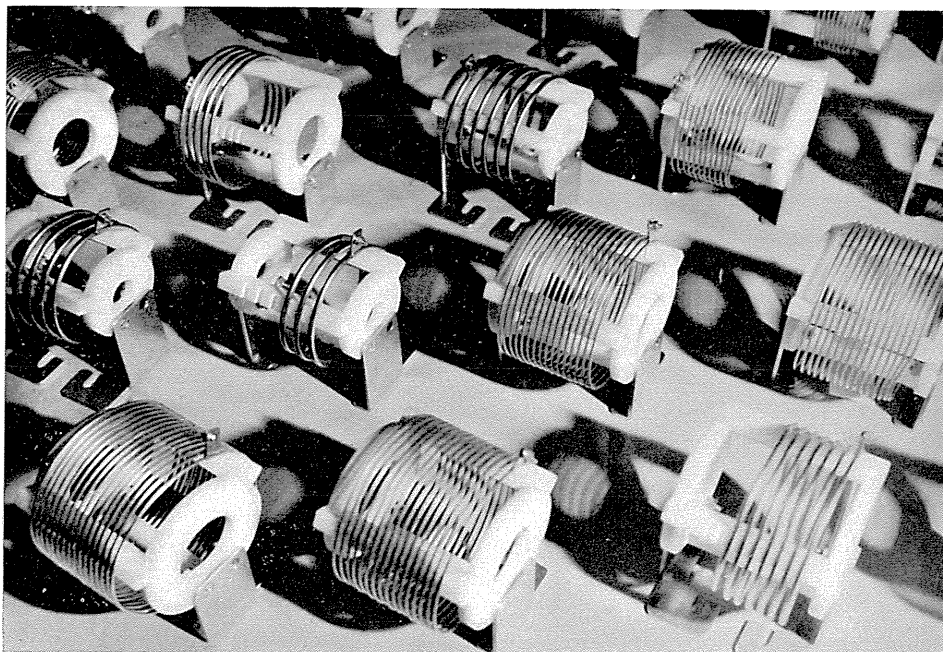


FIG. 5. Glass-bonded synthetic mica products. (Courtesy Mazda Laboratory of Tokyo-Shibaura Electric Co.)

*b. Hot-pressed mica*¹¹⁾²⁹⁾

When a mixture of the composition of fluor-mica is heated, the mixture reacts in the solid state and forms microscopic crystals of mica which aggregate in random orientation to form powder particles. Dense products made of pure mica can be made by pressing the mica powder at high pressures. The method of preparing hot-pressed mica was developed in the ETL and is being manufactured by Brush Beryllium Co., Cleveland, Ohio.

Optimum temperature and pressure for formation of hot-pressed mica depend on the composition of mica. Generally speaking, the lower the temperature employed for pressing, the higher the pressure necessary for obtaining a dense product. For example, fluor-boron-mica ($\text{KMg}_3\text{BSi}_3\text{O}_{10}\text{F}_2$) must be pressed at 70 kg/cm² for 60 min. at 980° C or 700 kg/cm for 60 min. at 750° C in order to be formed into a product having an apparent density of 2.6. At 3,500 kg/cm² only five minutes pressing was sufficient at 600° C to obtain the same dense product.

Graphite molds were used up to the pressure of 150 kg/cm² above 800° C. Inconel alloy was used as a mold material below 800° C and at higher pressures.

Properties of hot-pressed mica can be found in the ETL's reports. Dielectric constants and power factors of hot-pressed mica products at room temperature are shown in Table 3. Dielectric constants of these products did not change markedly when the temperature of the products was raised. However, power factors increased with temperature, especially showing rapid increase at about 250° C and above. Temperature dependence on power factor of hot-pressed synthetic mica compared with those of steatite, wollastonite, cordierite, and zircon ceramics was reported by Comeforo and Hatch.²⁹⁾

A breakdown voltage of hot-pressed synthetic mica is about 12 KV per mm. Other physical properties of this material are shown in Table 6.

TABLE 6. Physical Properties of Hot-Pressed Synthetic Mica*

Mechanical	Electrical
Specific gravity 2.5-3.5	Dielectric strength (KV/mm) 8-16
Water absorption (%) 0.05-10	Dielectric constant (1 MC) 5-8
Hardness (mohs) 2+-4+	Power factor (1 MC) (10^{-4}) 3-30
Safe operating temperature (°C) 700-900	
Coefficient of linear thermal expansion 20°-700° C (10^{-6}) 8-13	
Transverse strength (kg/cm ²) 700	
Compressive strength (kg/cm ²) <2450	

* Values from J. E. Comeforo, R. A. Hatch, R. A. Humphrey and Wilhelm Eitel, "Synthetic Mica Investigations: I, A Hot-Pressed Machinable Ceramic Dielectric," J. Am. Ceram. Soc., **36**, 286-294 (1953).

The coefficient of linear expansion of hot-pressed fluor-phlogopite is very close to that of iron. Thus the hot-pressed product was successfully brazed to copper. The brazed samples were proved to be vacuum tight.²⁵⁾

One of the important properties of hot-pressed synthetic mica is its easy machinability. Although hot-pressed mica is harder than block talc, intricate shapes may be machined from blocks in the same manner as from block talc using ordinary machine or hand tools.

Hot-pressed synthetic mica disk of 0.025 cm thickness and 1.0 cm diameter was found to withstand atmospheric pressure when the disk was placed on one end of a cylinder and the cylinder was evacuated. Applied to a small rectangular opening 0.16 cm by 0.37 cm, a sample of 0.006 cm thickness withstood atmospheric pressure. Disks as thin as 0.006 cm were obtained by grinding. Attempts to punch holes in thin disks of hot-pressed mica were unsuccessful.²⁵⁾

c) Reconstituted Mica

J. Bardet of France originated in 1939 a method of preparing pure mica foil from mica pulp made of pulverized natural mica suspended in water. This method was developed by H. George and L. Metzger and the reconstituted mica product "Samica" foil has been manufactured ever since 1949.

The process³⁰⁾ consists, first, of heating natural muscovite to remove part of its water of constitution and, second, a subsequent immersion of the heated mica while hot into a sodium carbonate solution. Next, the mica is drained and immersed in a dilute acid. Mica swells with simultaneous evolution of carbon dioxide gas and may attain a thickness a thousand times greater than its initial thickness. Agitating the solution suffices to gradually separate the mica leaflets, yielding a greasy-appearing pulp. This pulp is suspended in water, filtered, and dried; the product is a coherent foil of interlaced small mica leaflets. A continuous roll of foil may be made by a paper machine. The strength of the reconstituted mica foil is quite variable, depending on the type of mica used and on its treatment. The tensile strength of the foil may attain several kg per sq. mm. Varnishes may be incorporated to increase the strength of the foil. It was reported that electric properties of the reconstituted mica foil were superior on many points to those of mica "splitting" products.

According to Heyman, so called "virgin" mica leaflets, which are split in methanols, adhere strongly to each other and may be formed into a strong foil. The fact that freshly split mica crystals adhere to each other has been recognized in India for scores of years. This adhesive force is interpreted as being due to the residual electrostatic charges left when the mica is cleaved by breaking K-O bonds.¹⁸⁾

As synthetic fluor-mica can be formed into a dense and strong body by hot-pressing, it is expected it can be processed to form a strong foil of pure mica crystals. Experiments along this line were carried out at the ETL.³¹⁾ Split crystals of normal fluor-phlogopite were crushed in water down to sizes 1/4"-1/8" or smaller and mixed with fluor-boron-mica crystals in a blender. The resultant pulp was filtered and dried. Mica foils thus prepared were hot-pressed at temperatures of 1,000° to 1,300° C, for example, normal fluor-phlogopite foils containing 20% of boron-mica were hot-pressed at 1,300° C for ten minutes.

The power factor was 0.001 at room temperature and 0.002-0.003 at 300° C, the dielectric constants being 4.2-4.8 at room temperature. It seemed that hot-pressed mica was yet too weak for practical uses. The ETL people were trying to find a process obtaining stronger foil of reconstituted synthetic mica.

It was reported that Sylvania Electric Products Inc. carried out researches on reconstituted synthetic mica and obtained good results in using a vacuum tube spacer punched out of reconstituted synthetic mica foil.³²⁾

*d. Phosphate-bonded Mica*³³¹

In the manufacturing of refractories, phosphates are used as binding materials. The ETL people carried out experiments for preparing phosphate-bonded synthetic mica ceramics based on their experiences with preparations of phosphate-bonded talc.³⁴¹ Synthetic mica powder passed 80 mesh was thoroughly mixed with 5-15% of 85% H₃PO₄. The mixture was dry-pressed and fired for sintering.

As usual, as with press-formed ceramics, the strength of rupture and the apparent density of phosphate-bonded mica increase with the increase of molding pressure, while its water absorption and linear firing shrinkage decrease. However, phosphate-bonded boron-mica expanded when overburned, while phosphate-bonded normal fluor-phlogopite did not show overburning and had a wide range of firing temperatures. Electric properties of the product seemed to be unaffected by the addition of phosphoric acid, but affected by its own porosity. Power factors of phosphate-bonded mica were found to be of about the same order as those of hot-pressed mica having a similar porosity. Phosphate-bonded mica contains no glass and its small firing shrinkage and easy machinability are important characteristics, among others.

5. Conclusion

One of the most important characteristics of synthetic mica is its superior high temperature stability compared with natural mica. It can be prepared in a pure and homogeneous state. Also various types of substituted micas having various properties can be synthesized. Therefore, use of synthetic mica developed new fields of applications where natural mica could not serve. Several types of mica ceramics have been developed using powder crystals of synthetic mica.

Good yields of large single crystals have not been attained as yet; further researches and progress in the technique of manufacturing may improve the yield of large crystals. It is expected that synthetic mica crystal will prove its superior quality as a vacuum tube spacer and the like. Although synthetic mica manufacturer already established in Japan and in the United States are now producing mica ceramics using powder crystals of synthetic mica, it seems likely they are trying to prepare large single crystals for industrial uses.

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