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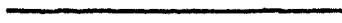
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THE DIELECTRIC PROPERTIES OF A SYNTHETIC FLUOR-MICA
FORMED BY GLASS-CERAMIC FABRICATION TECHNIQUES

227

BY
RAY F. SCHUMACHER, ^{red} 1962

51



A
THESIS

submitted to the faculty of the
UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN CERAMIC ENGINEERING

Rolla, Missouri

1965

115216



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ABSTRACT

A tetrasilicic fluor-mica, $K_2Mg_5Si_8O_{20}F_4$, was synthesized, utilizing glass forming techniques and subsequent heat treating of the mica glass. Discs, approximately two inches in diameter, were formed and heat-treated at selected temperatures between 700°C. and 1150°C. for various time periods. Density change, weight loss, shrinkage, and dielectric properties were measured to determine the characteristics of this material.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to his advisor, Dr. R. E. Moore, for his valuable suggestions during this investigation. The encouragement and moral support of Dr. D. E. Day, Professor G. E. Lorey, V. Burdick, and Dr. R. Gerson, are also gratefully acknowledged.

Many thanks are offered to my colleague, Mr. J. H. Ainsworth, who worked with me on the initial stages of the project.

The financial assistance of the Kaiser Refractory Company, in the form of a fellowship and research fund is gratefully acknowledged.

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I. INTRODUCTION

The natural micas are a group of sheet structure silicate minerals which owe their usefulness to a unique combination of physical, chemical, thermal, and dielectric properties. This combination of properties has created an important strategic demand for mica in the electrotechnical industries, and encouraged considerable research throughout the world pertaining to the production of synthetic mica.

Reports have been made on synthetic mica research dating back at least 100 years; however, during the last two decades there have been intensive research programs in Germany, Russia, Japan, and the United States. The largest program in this country was carried out at the U.S. Bureau of Mines, Electrotechnical Laboratory, Norris, Tennessee. Although the primary goal of producing large single crystals of mica was never fully realized, many important advances in the development and utilization of synthetic mica were achieved. Several new ceramic materials were studied, such as; hot pressed synthetic mica, reconstituted mica sheet, and phosphate-bonded mica. Other research in these fields has been carried out both by the government and private industry.

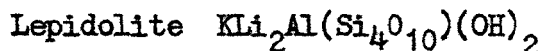
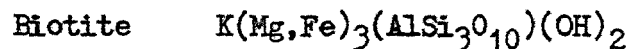
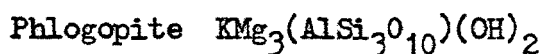
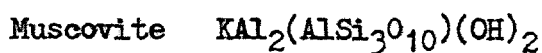
In 1964, Tuzzeo explored the development of a polycrystalline synthetic mica formed by glass-ceramic techniques. It was determined that synthetic mica could be produced by this method, and studies were carried out involving heat treatments of the glass and measurement of several dielectric properties.

The current investigation was conducted to further develop forming and heat treatment techniques, and study the dielectric properties of the resulting material at various temperatures. An attempt was also made to further understand the nucleation and crystallization of the glass to mica.

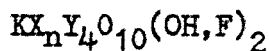
II. LITERATURE SURVEY

A. Classification and Properties of Natural Mica

Mica is the group name for a number of isomorphous minerals which are characterized by excellent basal cleavage, a high degree of flexibility, and toughness. The basic silicate structure of mica consists of SiO_4 tetrahedra linked by sharing three of the four oxygens, thereby forming a sheet structure.¹ The type of mica is determined by the presence of other ions in the structure as indicated by the four principle types of mica:

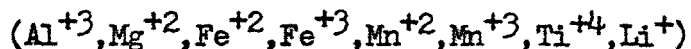


Further divisions in the classifications may be made if still other ions are present. A general formula, which has been found to fit all types of micas, is:

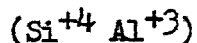


where $2 \leq n \leq 3$

cations of coordination number six = X,



cations of coordination number four = Y.



The potassium ions may be partially replaced by sodium and possibly to some extent by calcium.²

In this discussion, only the structure of phlogopite mica will be considered since it is representative of the other micas. The basic structure of mica consists of two sheets of SiO_4 tetrahedra with their vertices pointing toward the interior of the structure. The tetrahedra are linked together in one plane by sharing the three oxygen atoms which

form the base of the tetrahedron. In the phlogopite mica structure, one-fourth of the tetrahedra contain an aluminum atom instead of a silicon atom. The composition of the silicon-oxygen sheets then is $\text{AlSi}_3\text{O}_{10}$. At the center of each ring of six tetrahedra vertices lies an hydroxyl radical which may, in some cases, be replaced by a fluorine ion. A layer of magnesium ions may be situated between the two silicate sheets forming a firmly bound structure. The exterior of the silicate sheets possesses negative charges which may be compensated by potassium ions in twelve fold coordination. This ionic linkage between layers explains the greater hardness of the micas in comparison to talc and pyrophyllite in which the individual layers are uncharged and, therefore, have no cohesive forces.³ A schematic diagram showing the structure of phlogopite is given in Figure 1.⁴

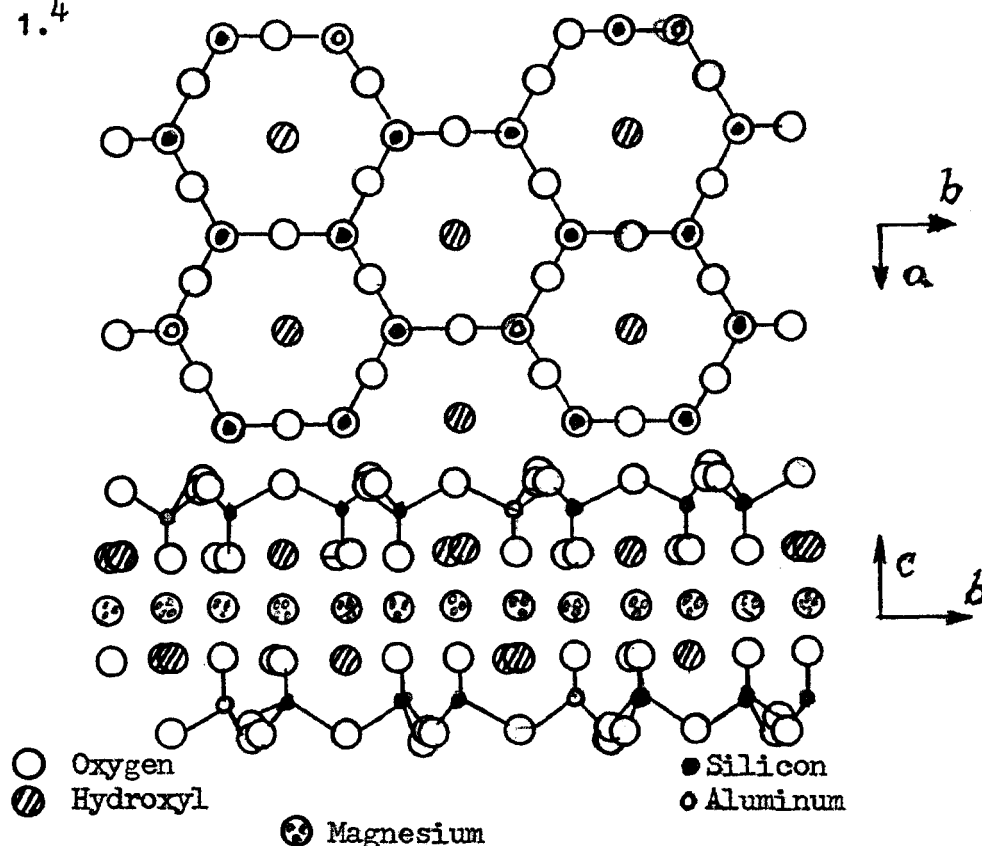


Figure 1. Crystal structure of phlogopite mica.

Many types of mica are capable of withstanding sudden and wide variations in temperature without any appreciable change in physical character. This is ascribed to their low coefficient of thermal expansion, ranging from 8×10^{-6} to 15×10^{-6} per $^{\circ}\text{C}$. parallel to the cleavage plane. Certain types of mica such as muscovite and fluor-phlogopite are resistant to thermal decomposition and can withstand temperatures up to 400°C . and $1,000^{\circ}\text{C}$. respectively.

Undoubtedly the most important properties of micas are their excellent electrical insulating qualities. One of these properties is the dielectric strength or the ability to withstand a large field strength without electrical breakdown. The dielectric strength of some micas is at least ten times greater than all other ceramic and organic insulating materials. It has been reported that high quality mica sheets can withstand from 2,000 to 6,000 volts per mil.⁴ with only a reduction of 10% to 20% up to 400°C . One other important characteristic of mica is its low power factor or the power which is dissipated in the material under an applied alternating field. It is this combination of high temperature stability and good electrical properties which makes mica a useful insulating and dielectric material.

B. Development of Synthetic Micas

The first successful synthesis of mica was the preparation of a biotite-like mica in 1887, and the feasibility of synthesizing various micas from the fluoro-silicate melts was established about 1888. The initial attempts at commercial synthesis were those of the Siemens-Schuckert Co. in Germany during World War I. Research apparently subsided until Gregoriev's mineralogical investigations in Russia revived interest in synthetic mica just before World War II. Active work on the problems of mica synthesis was undertaken in Germany about 1936 and in Japan about

1939. This research continued in Germany until late in 1944 when the disruption of technical facilities at the end of the war interrupted the work. In Japan, research on synthetic mica continues up to the present time.

Reports of the German work on synthetic mica stimulated interest in this country and a research program at the Bureau of Mines, Norris, Tennessee, was established. The initial objective of the program at the Bureau of Mines was to develop a substitute for strategic types of sheet mica used as dielectric insulators in various types of electrical equipment. Although such a material was never developed, it was clearly established that a series of isomorphic synthetic fluor-micas could be crystallized from the melt at atmospheric pressure. This was obviously more practical than trying to produce large quantities of hydroxyl micas in high pressure bombs or autoclaves. Over one hundred different micas were produced with varying physical and electrical properties.⁵

One of the first steps in the mica production was to determine a suitable crucible container for the highly corrosive fluorine melt. It was found that platinum, graphite, silicon carbide, and high silica fire-clay crucibles could be used; however, each had one or more disadvantages. Fire-clay crucibles containing 80% SiO_2 could be made more corrosion resistant if they were prefired to a semivitreous bond. A microscopic investigation showed that the melt reacted with the refractory to form a thin protective layer of highly viscous, high silica glass. The best melting process, however, utilizes internal resistance melting and the raw batch as its own container.

A study of raw materials⁶ was carried out in order to select materials which were plentiful, inexpensive, and had good characteristics as mica components. The preferred fluorine batch component was found to

be potassium silico-fluoride. It is manufactured as an unusually pure by-product of the phosphate fertilizer industry and is readily available in large quantities at a reasonable price. Due to its high reactivity, reaction with magnesia will start at temperatures as low as 500°C. The other components should not be used as hydrates, or if they are, the water vapor should leave at a low temperature. At higher temperatures the water vapor will combine with the fluorine aiding in the decomposition of the mica.

Several factors which inhibit fluorine losses from the melt are: tightness of enclosure, absence of water vapor in the raw materials, control of the furnace atmosphere, temperature and melting time, and a high degree of batch compaction. Two of the major decomposition products of tetrasilicic mica were found to be forsterite (Mg_2SiO_4) and norbergite ($Mg_2SiO_4 \cdot MgF_2$), which were formed due to varying degrees of volatilization of HF, SiF_4 , and KF. MgF_2 was found to be present when there was an excess of fluorine in the batch.⁷

A natural outgrowth of this study was to consider the properties of hot pressed synthetic mica.⁸ A fine grained ceramic material was formed by hot-pressing at 2,000 psi and 500°C. to 1250°C. at times up to 60 minutes. Although this is a rather expensive process, several worthwhile ceramics were produced. Several of the materials were soft enough to be sawed, drilled, turned, and otherwise worked with ordinary machine or hand tools. In addition, the hot pressed synthetic mica had excellent electrical insulating properties, possessing an extremely low dielectric dissipation and loss factor.

C. Glass-Ceramic Fabrication

Since the introduction of Pyroceram by Dr. S. D. Stookey in 1957, there has been considerable interest in the practice and theory of devitrification of glasses to glass-ceramics. By this process, the material is initially formed as a glass and later heat-treated below its melting point until it forms a crystalline ceramic material.

To be of any practical importance, this new process must have advantages over glass and sintered ceramics. The most desirable is that it should be possible to form an almost ideal polycrystalline structure, i.e., fine grained, uniform in grain size, randomly oriented, and free from pores and other imperfections. Also, one may hope for new crystal compositions and microstructures which will lead to new and useful physical properties.

Considering three different bodies of the same composition formed by glass, glass-ceramic, and sintering techniques, it is evident that each of the three bodies may have vastly different physical properties. When a glass is prepared, the resulting properties depend to a large extent on the composition, thermal history, and handling of the specimen, and less on the characteristics of the raw materials and details of the batching and melting procedure. However, when considering the properties of a sintered ceramic, the initial particle size and shape, raw material preparation, and firing cycle are of great importance. In many cases, the resulting physical properties are not dependent on the inherent properties of the crystals but of the voids, grain boundaries, and imperfections of the body. Glass-ceramic fabrication, however, combines the better parts of both techniques in that the resulting crystalline material is pore free and the initial character of the raw material is removed by the melting process.

The greatest contribution, however, to the physical properties of glass-ceramics is the minute, interlocking, non-oriented microstructure which may be achieved by this method. Studies made by electron microscopy, x-ray diffraction, and low angle x-ray diffraction have shown that efficient nucleation can produce particles as small as a few angstroms in size and that complete nucleation may be achieved with an average crystal size down to 200 to 300 angstroms. Further advantages include: improvements in strength, chemical durability, and uniformity of microstructure.⁹ An economic advantage is the adaptability of glass forming techniques, providing a product which is extremely uniform and inexpensive.

Several explanations for the crystallization mechanisms of the glass have been proposed. One prevailing view is that the catalyst dissolves in the melt and then precipitates as the glass is cooled to form nucleation sites for crystallization upon subsequent heat treatment.¹⁰ Another mechanism of crystallization in a catalyzed glass proposed by several workers^{11,12} is a liquid-liquid separation. During the cooling of a liquid glass melt, there is an aggregation process similar to that which causes crystallization in other melts. These aggregation processes take place at an intermediate stage between the ideal disorder of the melt and the order of the crystalline state. As cooling continues, clusters aggregate in certain areas to form the prerequisite stage for crystallization. Rapid cooling of the melt, however, leads to a congelation of amorphous phase in these areas which, in certain cases, will separate from the matrix phase in the form of droplets. The droplet shape is found in the phase possessing the highest surface tension.

In such cases, the structure of one vitreous phase may be better developed than that of the other. In several systems investigated, one phase would appear high in network formers, the other in network modifiers. The number and size of these clusters is basically dependent on the intensity of the field strength of the cations. By adding cations of high field strength, clustering can be increased.

Upon subsequent heat treatment, clustering continues and the catalyzing agent may form nuclei in the more developed phase, promoting crystallization. In general, the glass phase containing the network modifiers will crystallize since more network bridges are broken offering the greatest mobility to the modifiers. As crystallization continues, the droplets expand until finally crystallization of the material is complete.

Another distinct possibility has been suggested by Hillig and Chen^{13,14} to explain the crystallization of certain specific glasses. In these, the crystallization of the glass is an intrinsic property of the system, hence, there is no need for recourse to special catalyzing agents. Chen studied a synthetic phlogopite mica system and found that an intermediate pseudocrystalline phase was a prerequisite to the final crystallization. As the glass is heated a pseudocrystalline phase is heterogeneously nucleated and grows until the glass is completely converted to the intermediate phase. It is speculated that the potassium, magnesium, and fluorine ions are in a layer structure as in the mica, while the silicon-oxygen tetrahedra are still in the random arrangement as in the original glass. Mica crystals appeared to form first at the interfaces between the new phase and the parent glass and subsequently grew into the intermediate phase.

The factors favoring such a two step change can be explained structurally and thermodynamically. The energy barrier involved in transforming the glass to a slightly rearranged pseudocrystalline phase is apparently smaller than that required to transform the glass to a mica crystal directly. The proposed structural similarity between the pseudocrystalline phase and the parent glass also suggests that the interfacial energy between these two would be less than that between the glass and mica crystals. In this way, the free energy barrier to crystallization is lowered and crystallization may proceed more easily.

D. Dielectric Properties of Materials

1. Theoretical Macroscopic Approach

If an electric potential is applied to two parallel plates in a vacuum, the quantity of charge which may be stored on the plates is proportional to the voltage,^{15,16}

$$Q = C_0 V \quad (1)$$

where C_0 is the proportionality constant or capacitance in a vacuum. By taking the derivative with respect to time,

$$dQ/dt = C_0 (dV/dt) = I_c \quad (2)$$

where dQ/dt is the current, I_c , which is charging the capacitor.

When a sinusoidal voltage is applied as the voltage source,

$$V = V_0 e^{j\omega t} \quad (3)$$

where $\omega = 2\pi f$ and $j = (-1)^{\frac{1}{2}}$,

or

$$V = V_0 (\cos \omega t + j \sin \omega t). \quad (4)$$

By solving for I_c from (2) the current becomes,

$$I_c = C_0 dV/dt = j\omega C_0 V \quad (5)$$

$$I_c = C_0 V_0 \omega (-\sin \omega t + j \cos \omega t). \quad (6)$$

When the charging current and voltage are plotted on real and imaginary axis as in Figure 2, the charging current will lead the applied voltage by 90° .

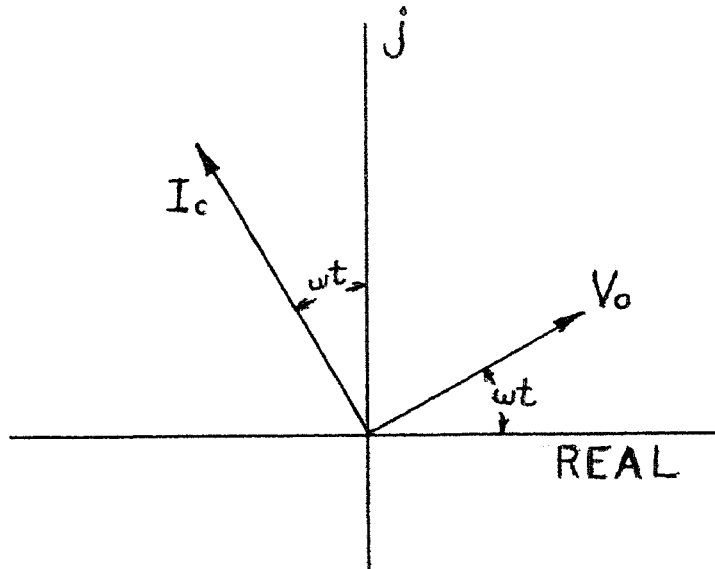


Figure 2. Schematic of current and voltage in a capacitor.

The capacitance term, C_o , contains a geometrical and a material factor,

$$C_o = (A/d) \epsilon_o \quad (7)$$

where A is the area of the parallel plates and d is the distance between them. ϵ_o is the dielectric constant or permittivity of a vacuum. If a given material of dielectric constant ϵ' is inserted between the plates, there will be an increase in the capacitance,

$$C = C_o \epsilon' / \epsilon_o = C_o K' \quad (8)$$

where K' is the relative dielectric constant.

When we consider real materials in alternating fields, there will appear in addition to the charging current a loss current given by,

$$I_l = G V \quad (9)$$

where G represents the conductance of the dielectric.

The total current is expressed by,

$$I = I_c + I_l = (j\omega C + G) V. \quad (10)$$

The loss current appears in Figure 3 as a retardation in I where the current leads the voltage by an angle less than 90° .

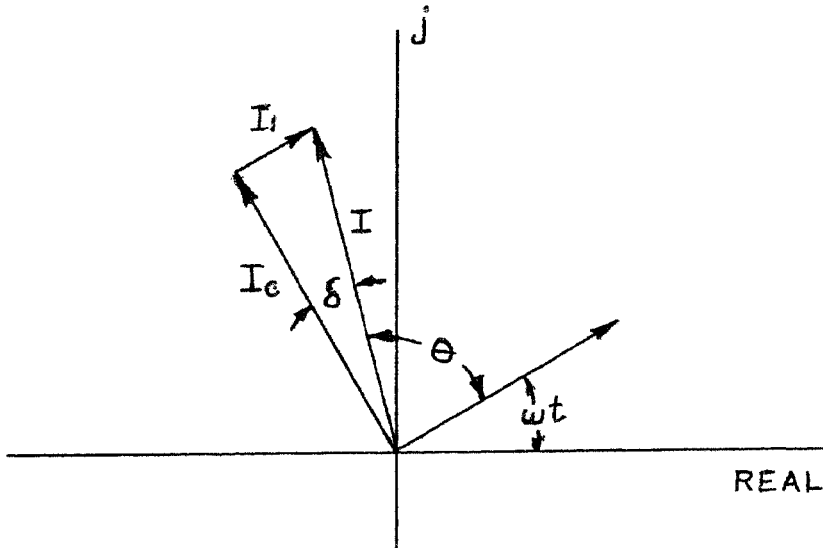


Figure 3. Schematic of loss current and voltage in a capacitor.

The dissipation factor D is given by Eq. 11 where δ is the loss angle.

$$D = \tan \delta = \cot \theta = I_l / I_c = 1/\omega RC \quad (11)$$

The losses in a capacitor may be expressed in a circuit diagram by a resistor and a capacitor in parallel.

Since the conductance term of a capacitor need not stem from a migration of charge carriers only, but may include any other energy consuming process, it has been customary to introduce the complex permittivity,

$$\epsilon^* = \epsilon' - j \epsilon'' \quad (12)$$

where ϵ'' is the loss factor. The loss tangent then becomes

$$\tan \delta = \epsilon'' / \epsilon'. \quad (13)$$

Another term frequently utilized is the power factor, or the ratio of the power dissipated in the capacitor to the product of the sinusoidal voltage and current,

$$PF = P_d / V \cdot I = \cos \theta = \sin \phi \quad (14)$$

2. Microscopic Approach

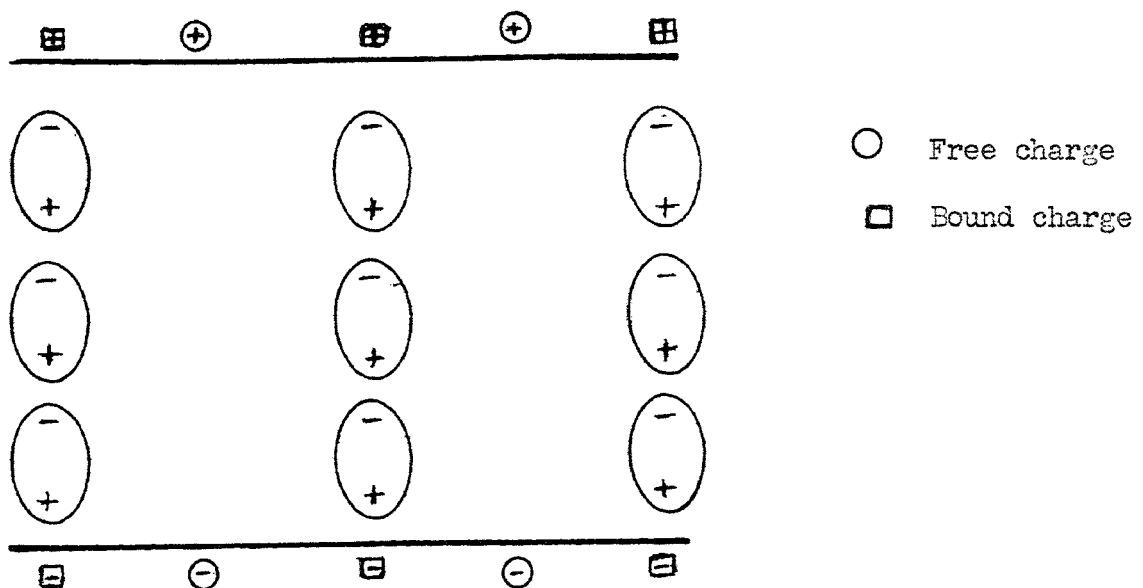
A dielectric material increases the storage capacity of a condenser by neutralizing charges at the electrode surface. Only a fraction of the total charge is considered as a voltage difference between the plates. Originally in a vacuum,

$$V = Q/C_0 \quad (15)$$

but with a dielectric material,

$$V = \frac{Q/K}{C_0} \quad (16)$$

It is much easier to visualize this as the action of a series of dipole chains extending throughout the material as shown in Figure 4.



Each dipole possesses a moment given by the product of the charge Q and the distance separating them,

$$\mu = Q d. \quad (17)$$

The average dipole moment $\bar{\mu}$ may be assumed to be proportional to the local electric field strength E that acts on the particle,

$$\bar{\mu} = \alpha E. \quad (18)$$

The proportionality factor α , is called the polarizability.

There are four distinct mechanisms of polarizability in real materials. The first is the electronic polarization or the displacement of the electron cloud away from the nucleus. By the displacement of charged atoms or groups of atoms with respect to each other, a second type of induced dipole moment is created called atomic polarization. This is the displacement of ions of opposite sign from their regular lattice positions. A third type, which is mainly concerned with liquids and molecular solids is the orientation polarizability. This orientation polarization can also occur in crystals and glasses when two or more equivalent positions are available. Finally, many times there are charge carriers which can migrate some distance through the dielectric. When such carriers are impeded in their motion by interfaces or traps, they create a space charge which appears as an increase in capacitance of the sample. This is known as space charge or interfacial polarizability. Assuming that each of the mechanisms act independently,

$$\alpha = \alpha_e + \alpha_a + \alpha_o + \alpha_s. \quad (19)$$

The electronic polarizability contributions are always present and are the main contributors in the optical range of frequencies. By a comparison of two equations, the Lorentz and Mosotti equations, it may be shown that the relative dielectric constant in this frequency range is equal to the index of refraction squared¹⁹,

$$\kappa_e = N^2. \quad (20)$$

Dielectric materials are used over a wide range of frequencies, temperatures, and environmental conditions. The changes in dielectric constant and loss factor with frequency are produced by the dielectric polarizations of the material. Starting at the highest frequency, the dielectric constant is proportional to the electronic polarizability. At lower frequencies each succeeding polarization adds its effect to the dielectric constant as shown in Figure 5. The dielectric constant is greatest at zero frequency. Each increase in polarization furnishes a maximum of both loss factor and dissipation factor. The frequency, at which the loss factor is a maximum is called the relaxation frequency for that polarization. Any d-c conductance caused by free ions or electrons, while having no effect on the dielectric constant, will produce a dissipation factor which varies inversely with the frequency.¹⁷

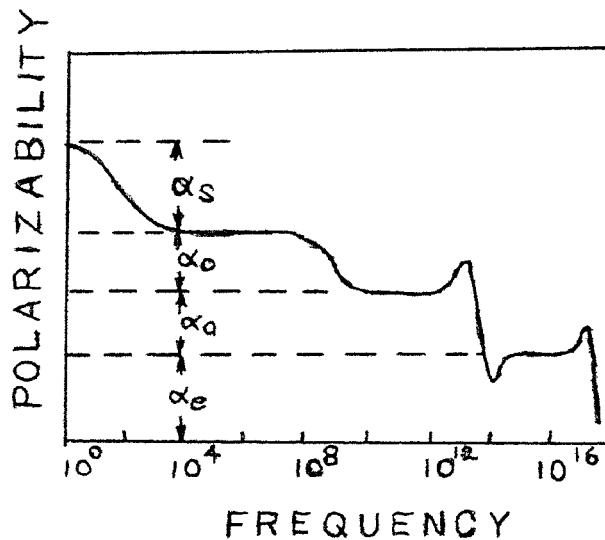


Figure 5. Polarizations

The major electrical effect of temperature on an insulating material is to increase the relaxation frequencies of its polarization. The losses increase exponentially with temperature due to increases in ion mobility, crystal imperfection mobility, and d-c conductivity.

Humidity will greatly increase the magnitude of the interfacial polarization thus increasing the dielectric constant, loss factor, and the d-c conductance. These effects of humidity are caused by absorption of water into the volume of the material and adsorption of an ionized water film on the surface.

E. Physical and Electrical Properties of Tetrasilicic Fluor-Mica

Some of the properties of tetrasilicic fluor-mica, ($K_2Mg_5Si_8O_{20}F_4$), were determined at the Bureau of Mines, Norris, Tennessee. The unit cell dimensions and the x-ray density are given in Table I.⁶

TABLE I.

Physical Constants of Tetrasilicic Fluor-Mica

<u>Unit Cell Dimensions</u>				<u>X-ray Density</u>
<u>a₀</u>	<u>b₀</u>	<u>c₀</u>	<u>B</u>	<u>(g./cc.)</u>
5.218	9.160	20.105	95.000	2.835

A sample of tetrasilicic mica was provided by the Bureau of Mines, Norris, Tennessee. X-ray diffraction data obtained by Tuzzeo, using a Norelco, Model 12045, diffractometer, gave the interplanar spacings and estimated intensities listed in Table II.²⁰

TABLE II.

X-ray Diffraction Data of Bureau of MinesTetrasilicic Fluor-Mica

<u>d (Å)</u>	<u>Intensity</u>
9.80	VS
4.95	S
3.68	VVW
3.61	VVW
3.31	VS
3.12	M
2.89	M
2.69	W
2.60	W
2.50	M
2.40	W
2.15	W
1.99	S
1.656	M
1.525	W
1.428	M
1.410	W
1.353	W
1.306	VW
1.250	M
1.220	VVW
1.210	VVW

V = Very; W = Weak; M = Medium; S = Strong

A study of the characteristics of hot pressed synthetic mica was carried out at the Bureau of Mines and the results are given in Table III.⁵

TABLE III.

Characteristics of Hot Pressed Tetrasilicic Mica

Machinability	Good
Apparent Porosity	2.0 - 5.4
Dielectric Constant	4.5 - 5.1 @ 10^6 cps
Power Factor	.010 - .002 @ 10^6 cps
Loss Factor	.009 - .054 @ 10^6 cps

In a study of the dielectric properties of tetrasilicic mica bonded with 10% phosphoric acid, the following results were obtained at 10^6 cps and are shown in Table IV.⁶

TABLE IV.

Dielectric Properties of Phosphate-Bonded Mica

<u>Tem. (°C)</u>	<u>K</u>	<u>Power Factor</u>
Rm. Temp.	3.83	.0030
100	3.84	.0031
150	3.85	.0035
200	3.86	.0049
250	3.86	.0083
300	3.93	.0130
350	4.00	.0190

Tuzzeo determined that it was possible to form tetrasilicic synthetic mica by glass-ceramic fabrication techniques. The density of the glass was determined and reported as 2.56. After heat treatment, the material was identified by x-ray diffraction and definitely determined to be tetrasilicic mica. The dielectric properties of several specimens were determined and are given in Table V. Samples heat treated at 620°C. to 800°C. had dielectric loss factors comparable to other commercial insulating materials.²⁰

TABLE V.

Dielectric Constant and Loss at one Megacycle

<u>Heat Treat.</u> (Temp. °C.)	<u>Constant</u> (K)	<u>Loss</u> (Tan)
620	6.71	.0033
630	6.40	.0035
640	6.35	.0032
690	6.18	.0027
800 - 1 hr.	6.06	.0010
1000 - 3 hrs.	6.00	.0152

III. EXPERIMENTAL PROCEDURE

A. Raw Materials and Batch Preparation

It was initially decided to use the same raw materials as were used by Tuzzeo. The materials were: potassium silicofluoride, K_2SiF_6 , from U.S. Phosphoric Products, a division of Tennessee Corp., Tampa, Florida; silica, SiO_2 , from Ottawa Flint Co., Ottawa, Illinois; light magnesium carbonate, $Mg_4(OH)_2(CO_3)_3 \cdot 3H_2O$ and potassium carbonate, K_2CO_3 , both from Fisher Scientific Co. All raw materials were -200 mesh particle size or finer.

The batch composition was calculated from the mica formula but with 10% excess fluorine. The raw materials, batch equivalents, batch weights, and oxide percentages are listed in Table VI.

TABLE VI.

Batch Formula for $K_2Mg_5Si_8O_{20}F_4$

<u>Raw Materials</u>	<u>Batch Equivalents</u>	<u>Batch Weights</u>	<u>Oxide Percentages After Melting</u>
K_2SiF_6	.122	73.95	19.6
K_2CO_3	.044	209.10	24.4
$MgCO_3$ (light)	.208	16.90	3.0
SiO_2	1.211	200.00	52.9

The raw materials were either dried or kept in tightly sealed plastic containers until they were weighed to the nearest .01 g. on a two pan torsion balance. Thorough mixing was accomplished in a twin shell V-blender for one hour. Shorter mixing times resulted in non-

homogeneity of the glass. Batch segregation and fluorine losses in the melt were reduced by pressing the batch into 50 g. pellets. These were then dried at 500°C. for one-half hour.

B. Fusion of the Raw Material

Containers for the melt were of high silica fire clay, prefired for one-half hour to improve their corrosion resistance. Melting of the raw material was performed in a top loading, electric, resistance furnace, equipped with silicon carbide heating elements. Pellet charges weighing approximately 250 g. were placed in the furnace and soaked for 45 minutes at 1300°C.

C. Sample Formation

After smelting for 45 minutes at 1300°C., 20 g. of melt were poured into a machined graphite mold which had been preheated to 500°C. The glass was pressed into a disc 2 inches in diameter and 1/8 inch thick. After pressing, 10 to 15 seconds elapsed before the glass disc could be removed from the mold and placed on a small turn-table inside a 500°C. muffle furnace. The turn-table allowed removal at the furnace opening and cooling at the rear of the chamber. The discs were then annealed at this temperature.

This forming process was found to be extremely difficult on a laboratory scale. If the discs were thin or cooled too rapidly, they shattered; however, if they were thick or cooled too slowly the glass would crystallize spontaneously. Mold design was a critical factor; the mold should; (1) not constrict the specimen, (2) allow easy removal of the samples, and (3) give a sample thickness between 1/4 to 3/8 in.

D. Heat Treatment of Samples

All heat treatments of the glass were conducted in an electric Harrop Box Furnace, utilizing two of the three rates available. The medium rate was used to 800°C . and the high rate above this temperature. If the medium rate was not followed up to 800°C ., cracking occurred in the samples. The heating schedule is reproduced in Figure 6.

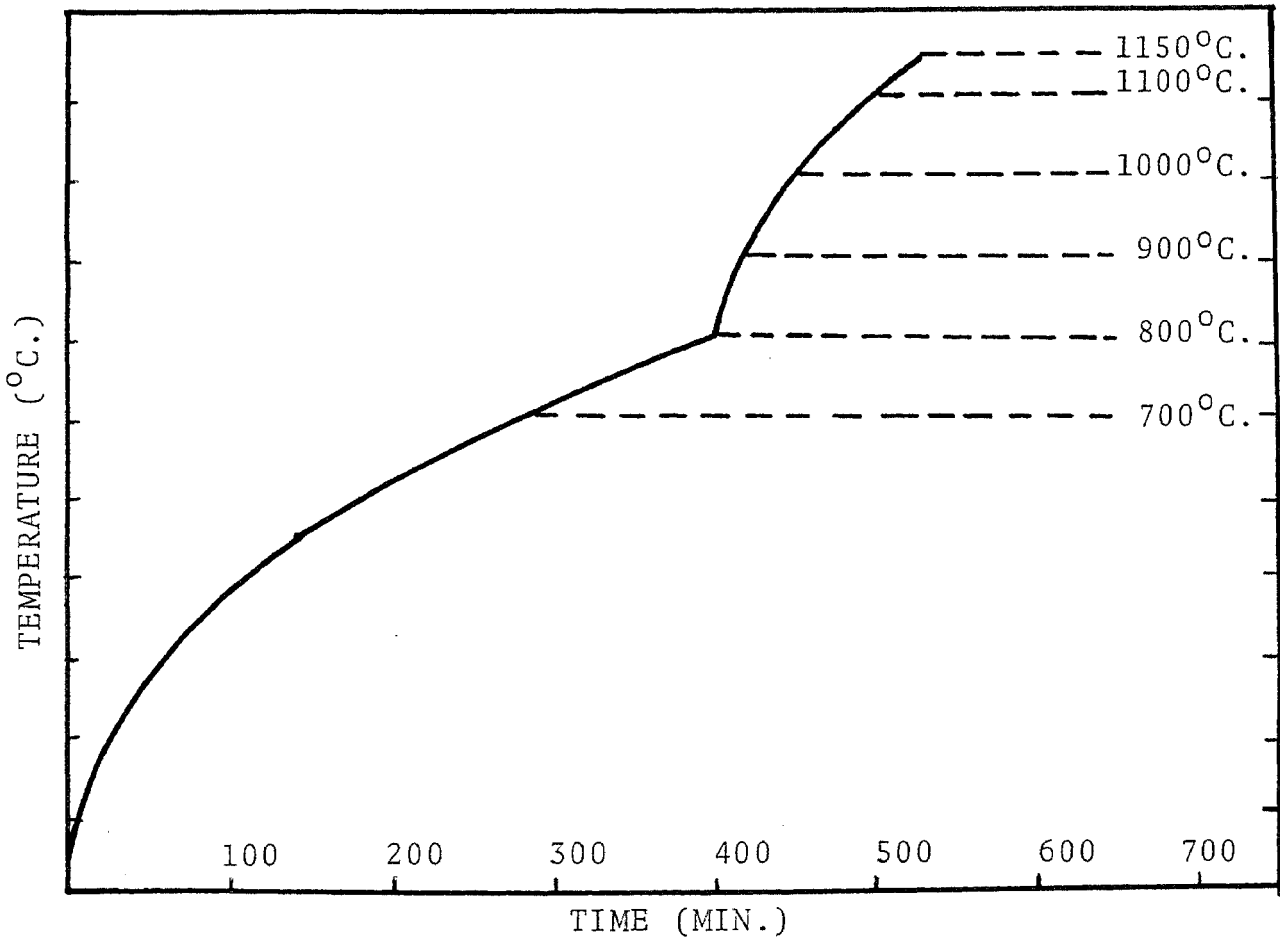


Figure 6. Heat treatment schedule.

E. Density Measurements

The densities of the samples before and after heat treatment were measured. The samples, having been dried overnight at 106°C ., were measured on a Mettler electric precision balance. The samples were then soaked in distilled water under vacuum for three hours and weighed suspended in water. Densities were calculated from equations derived from the Archimedes Principle. Diametral and axial measurements were also recorded

to determine changes in dimensions after heat treating.

F. X-Ray Determinations

X-ray samples were ground to -200 mesh particle size and dried at 106°C. A General Electric XRD-5 x-ray diffraction unit, emitting Cu-k α radiation and scanning at 2 degrees 2 θ per minute, was utilized for all x-ray determinations. A logarithmic scale of intensities was employed to increase sensitivity in detecting minor phases. All patterns were compared to a standard sample of tetrasilicic mica from the Bureau of Mines, Norris, Tennessee.

G. Dielectric Sample Preparation and Measurement

The samples were ground flat on one side before being mounted on glass slides. This was necessary in order to utilize an Ingram-Ward thin section grinder which could produce samples parallel to within .003 in. Specimens were removed from the glass slides and thickness and diameter measurements were taken. Silver electrodes were made by coating the samples with Du Pont air-drying conductive cement No. 8030. It was necessary to use air-drying cement rather than the usual fired-on silver, due to a reaction of the silver and fluorine at temperatures above 500°C. By polishing the air-dry cement with a small cloth and alumina powder, however, satisfactory electrodes having resistances less than .1 ohm were produced. Several commercial samples of insulating materials were prepared to study differences in electrode preparation and insure standardization of this technique. These samples were obtained from: Diamonite Mfg. Co., Shreve, Ohio; Coors Porcelain Co., Golden, Colorado; American Lava Corp., Chattanooga 5, Tennessee; and Molecular Dielectrics Inc., Clifton, New Jersey.

All samples were dried at 120°C . overnight and cooled in a dessicator before being placed in a small Huppert electric furnace. A platinum stand was used to support the specimen, while a movable platinum wire served as the high lead. A standardized chromel-alumel thermocouple, in conjunction with a Leeds and Northrup potentiometer, was used to measure the temperature of the furnace. The micas, only, were preheated to 300°C . for half an hour to insure dryness. A deliquescent agent was used to prevent pick-up of water at the lower temperatures. The samples were held at the desired measurement temperature for 10 to 15 minutes before the furnace was turned off and the dielectric properties were measured. In two studies of the glass-pseudocrystalline phase change, a constant rate of 2°C . per minute was used between measurement temperatures. The sample was not held at any temperature.

A General Radio 1610-B2 capacitance measuring assembly was used to measure the dielectric constant and dissipation factor at 100 kc. and 45 volts ac. The substitution method²¹ was utilized, thereby reducing the errors due to lead wires, internal circuit elements, and allowing measurement of capacitances below 100 mmf. By this method, the bridge is initially balanced with the high lead disconnected, then with the unknown sample in the circuit the bridge is rebalanced. The capacitance and dissipation factor may then be calculated from the following formulas:

$$C_x = \Delta C \quad (22)$$

where $\Delta C = C' - C \quad (23)$

$$D_x = (C'/C) \Delta D \quad (24)$$

where $D = (D - D') f/f_0 (.01). \quad (25)$

The primed letters designate the initial readings, with the sample disconnected from the rest of the circuit, and f and f_0 are the frequencies of the oscillator and range selector respectively. The dielectric constant may then be calculated by,

$$K = 4.45 t C_x/A \text{ (mmf, in)} \quad (26)$$

where t is the thickness and A is the area. Resistivity measurements were taken in a similar fashion with a Kiethly 610-A Electrometer.

H. Preparation of Polished Sections

Samples, which had been heat-treated for $100^\circ\text{C}.$ -3hrs., $1100^\circ\text{C}.$ -4 days, $1150^\circ\text{C}.$ -1 day, and $1150^\circ\text{C}.$ -6days, were mounted in bakelite and were ground and polished using a Buehler automatic polishing apparatus. Grinding was accomplished with 320, 400, and 600 grit abrasive papers. One-half micron Al_2O_3 on an A-B Metcloth was used for final polishing. Each sample was etched for 10 seconds in a 10% solution of HF and immediately rinsed with tap water.

The technique of reflected light microscopy, using a Bausch and Lomb Metallograph, was adopted for this study. A representative section of each sample, as viewed under the microscope at 500x magnification, was photographed using Kodak metallographic plates. Magnification of the photomicrographs is 500x.

IV. EXPERIMENTAL RESULTS

A. X-Ray Diffraction Studies of Heat-Treated Mica-Glass

X-ray diffraction studies indicated that the glass possessed short range order evidenced by two broad diffraction peaks. At heat treatment temperatures as low as 700°C. for 3 hours, a number of broad peaks appeared with the observed diffraction lines shifted slightly from the respective mica spacings. These peaks relate to a pseudocrystalline phase which possesses some of the ordering of the crystalline state. Heat treatments for 3 hours at 800°C. produced increases in the intensities of some of the diffraction peaks, while it shifted others to coincide with the mica d-spacings. This suggested the beginning of mica crystallization from the pseudocrystalline phase. No significant difference could be detected between the diffraction patterns for a 3 hour and for a 4 day heat treatment at 800°C.

Most of the diffraction peaks of tetrasilicic mica were present after intermediate heat treatments at 900°C. and 1000°C. Diffraction lines generally increased in number and intensity with heat treatments at higher temperatures, until devitrification at 1150°C. for 1 day produced all the interplanar spacings of tetrasilicic mica. Extended heat treatment at 1150°C. for 6 days, produced a specimen which compared quite closely in respective diffraction lines and intensities with the sample from the Bureau of Mines, Norris, Tennessee. Decomposition phases, such as norbergite or forsterite, as reported by the Bureau of Mines, could not be detected in the extensively heat-treated material.

B. Microstructure of the Heat-Treated Mica-Glass

A short discussion of the observed visual changes of the heat-treated samples may be of some significance. No noticeable difference could be seen between the pseudocrystalline sample, (700°C. for 3 hrs.), and

the original glass. The samples heated above 800°C . had a translucent white appearance, with translucency decreasing with higher temperature heat treatments. After heat treatments at 1150°C ., an opaque white material with visible crystals at the fracture surfaces was produced. The microstructures of samples after heat treatments at: 1100°C . for 3 hrs., 1100°C . for 4 days, 1150°C . for 1 day, and 1150°C . for 6 days are shown in Figures 7, 8, 9, and 10.

A glass sample, after heat treatment at 1100°C . for 3 hours, exhibited a homogeneous array of extremely small crystals. Glass or pseudocrystalline phases could not be distinguished. Heat treatment at 1100°C . for 4 days produced numerous small crystals and several large ones approximately 10 microns in length. After heat treatment for 1 day at 1150°C ., better defined crystals of approximately 20 microns in length were produced. The extended devitrification at 1150°C . for 6 days developed extremely large, well defined lath-shaped crystals approximately 100 microns in the longest direction.

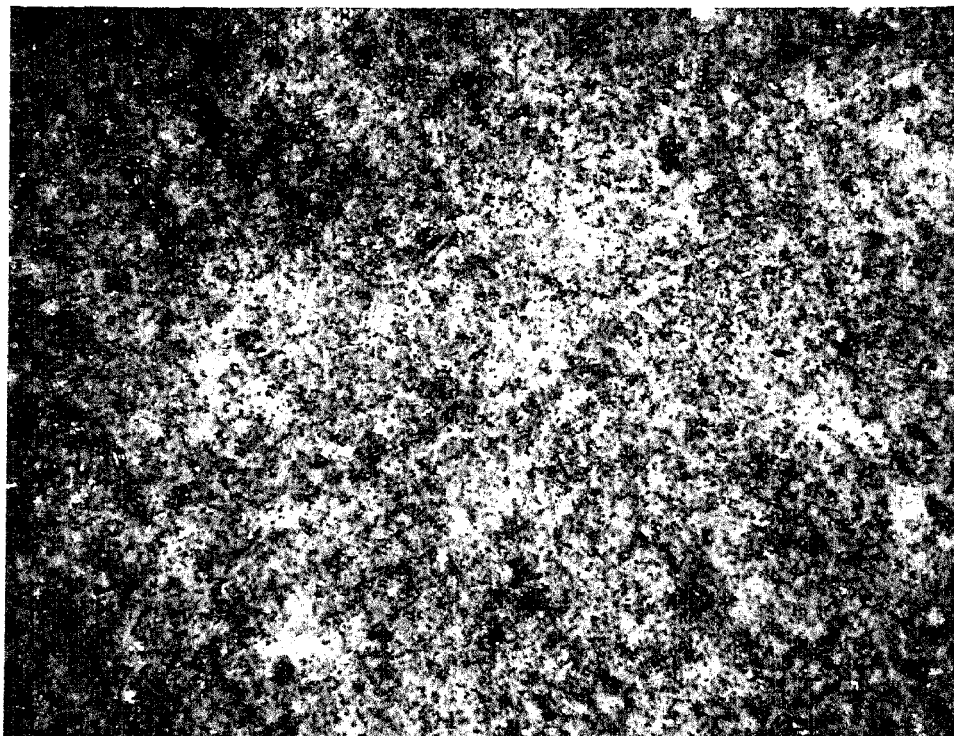


Figure 7. 500x. Heat-treated at 1100°C. for 3 hours.

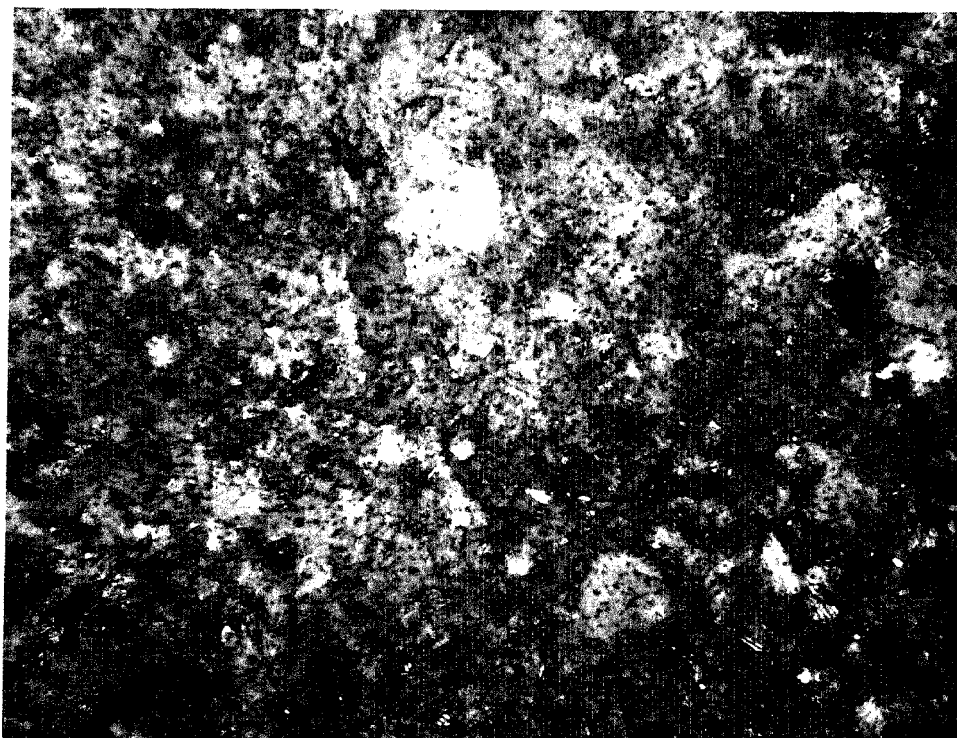


Figure 8. 500x. Heat-treated at 1100°C. for 4 days.

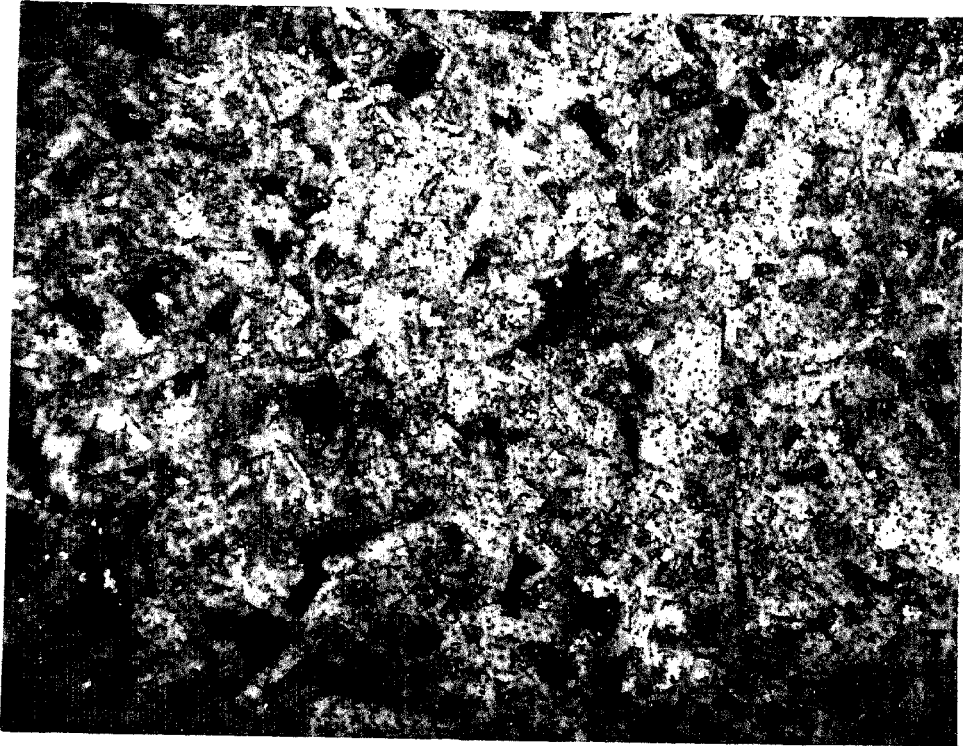


Figure 9. 500x. Heat-treated at 1150°C. for 1 day.

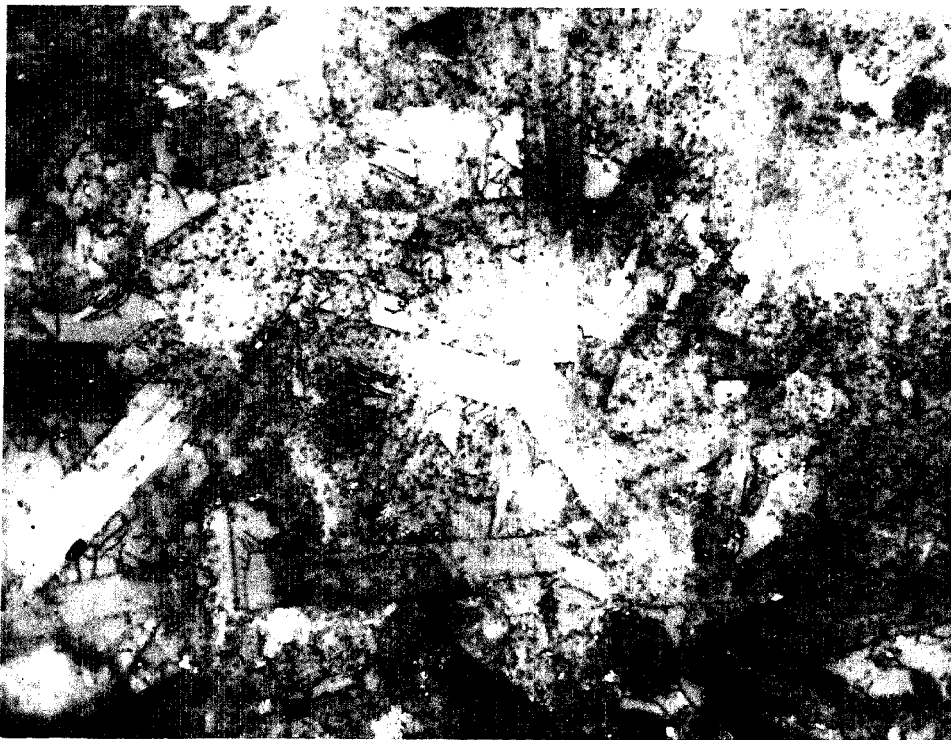


Figure 10. 500x. Heat-treated at 1150°C. for 6 days.

C. Physical Measurements of the Heat-Treated Mica-Glass

A study was conducted of the physical changes resulting from the effects of heat treatments upon the mica-glass. Weight loss measurements were taken to determine the extent of decomposition during devitrification. Diametral dimension measurements and densities of disc-shaped specimens were utilized in an attempt to follow structural changes. No physical changes were detected at temperatures below 600°C. The data for samples heat-treated above 600°C. are reported in Table VII.

TABLE VII.

Physical Changes Due to Heat Treatment

<u>Heat Treatment</u>	<u>Average Weight Loss (%)</u>	<u>Average Diametral Change (%)</u>	<u>Average Density (g./cc.)</u>
700°C. - 3hrs.*	0.000	1.76	2.712
800°C. - 3hrs.	0.003	2.62	2.766
900°C. - 3hrs.	0.012	2.71	2.803
1000°C. - 3hrs.	0.006	2.48	2.839
1100°C. - 3hrs.	0.037	1.79	2.799
1150°C. - 3hrs.	0.060	0.92	2.746
800°C. - 4days	0.010	2.82	2.801
900°C. - 4days	0.032	2.83	2.834
1000°C. - 4days	0.027	2.50	2.810
1100°C. - 4days	0.400	1.07	2.751
1150°C. - 4days	0.461	0.81	2.724
1150°C. - 3hrs.	0.060	0.92	2.746
1150°C. - 1day	0.236	0.82	2.738
1150°C. - 3days	0.325	0.48	2.731
1150°C. - 4days	0.461	0.81	2.724
1150°C. - 6days*	0.870	0.25	2.716

* Only one specimen available for measurement.

Weight losses generally increased with increasing devitrification temperatures and times. Weight losses, at intermediate heat treatments of 1100°C . for 3 hours and 900°C . for 4 days, were only .037% and .032%. It is believed that these low weight losses would not affect the properties of the devitrified material. However, the weight loss of 0.87%, observed in the extended heat treatment at 1150°C . for 6 days, undoubtedly reflects compositional changes.

Diametral shrinkage and density both followed the same general trends. Density and shrinkage increased rapidly above 600°C . and reached maxima at the intermediate temperature heat treatments at 900°C . and 1000°C . The maxima in density closely approached the theoretical density of tetrasilicic mica, i.e., 2.835 g./cc. Expansion in the specimens began at temperatures above 1000°C . causing a decrease in the density. The lowest density observed was 2.716, after the 1150°C . for a 6 day heat treatment.

D. Dielectric and Resistivity Measurements

1. Measurements of Commercial Ceramic Materials

A number of commercial ceramic insulating materials of various dielectric grades were measured to standardize the procedure and develop testing techniques. All dielectric measurements made by this investigator were at 100 kc. Measurements at this frequency are more sensitive to conductivity losses than those at higher frequencies. The dielectric constant and dissipation factor measurements of the materials, as reported by their manufacturers, are for 1 megacycle and will, therefore, be lower than the measurements made in this laboratory at 100 kc. These materials and their room temperature dielectric properties are listed in Table VIII, and the measured dielectric properties up to 400°C . are reported in Figures 11, 12, and 13.

TABLE VIII.

Comparison of Manufacturers Specification and LaboratoryMeasurements

Material			Manufacturers Typical Values @ 25°C., 1mc.	Measured Values @ 25°C., 100kc.
American Lava Corp.				
Alsimag	576	85% Al ₂ O ₃	K = 8.3 D = .0004	9.0 .0009
"	614	96% "	K = 9.1 D = .0003	9.9 .0007
"	748	98% "	K = 9.2 D = .0002	9.8 .0003
"	753	99% "	K = 9.6 D = .0002	9.8 .0007
"	202	Cordierite	K = 5.0 D = .0040	4.5 .0098
"	665	Steatite	K = 6.3 D = .0008	6.6 .0013
Diamonite Products Mfg. Co.				
Diamonite	p - 3864	95 - 97% Al ₂ O ₃	K = 8.7 D = .0005	9.7 .0005
"	p - 3142	" "	K = 9.6 D = .0005	9.75 .0008
Coors Porcelain Co.				
Coors	AD - 96	96% Al ₂ O ₃	K = 9.0 D = .0001	9.2 .0006
Molecular Dielectrics Inc.				
Mykroy	750	Glass	K = 7.1 D = .0014	8.2 .0014
"	1100	Bonded Mica	K = 7.5 D = .0015	7.1 .0025

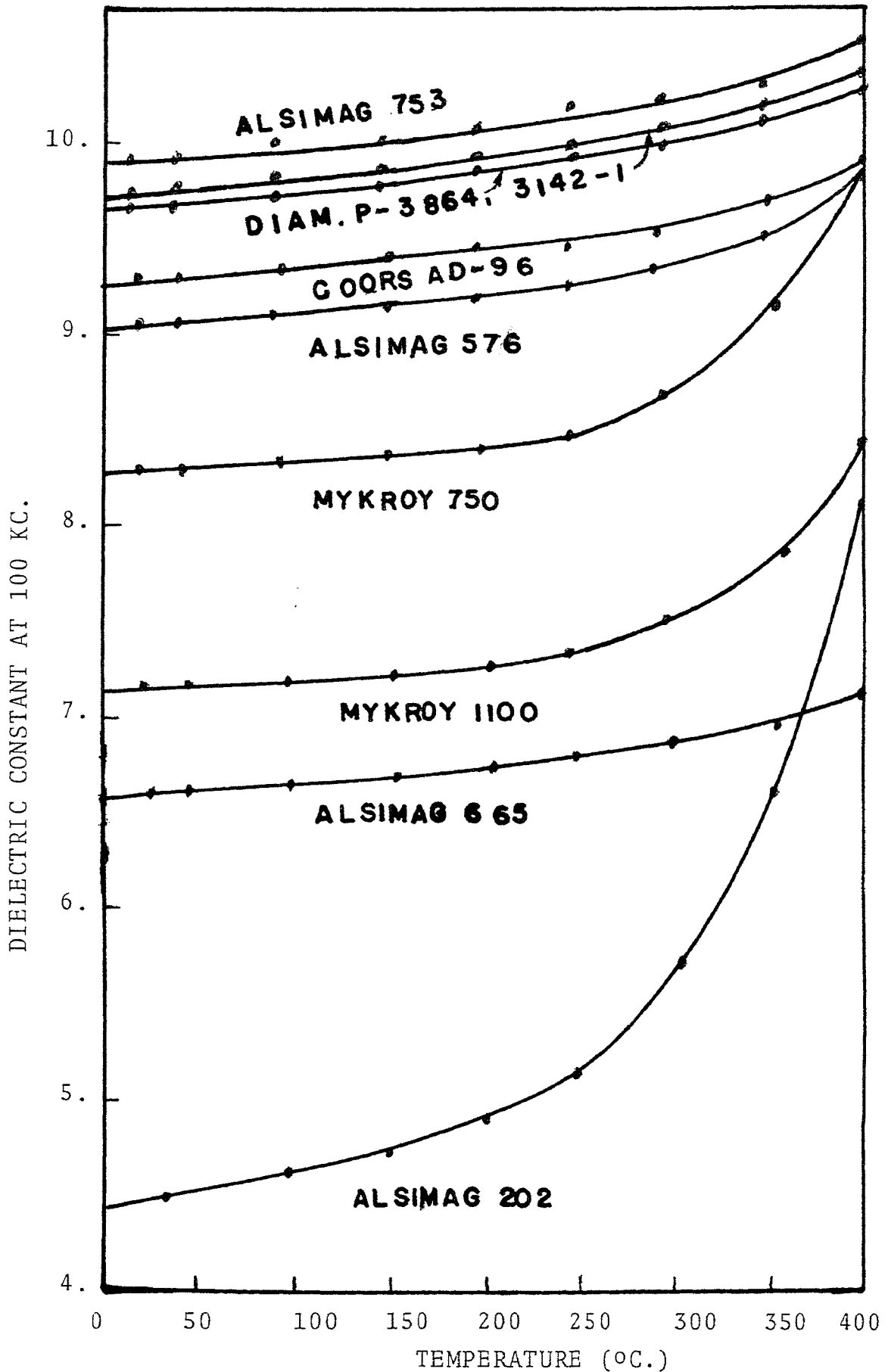


Figure 11. Observed dielectric constant, temperature relationships of commercial insulators.

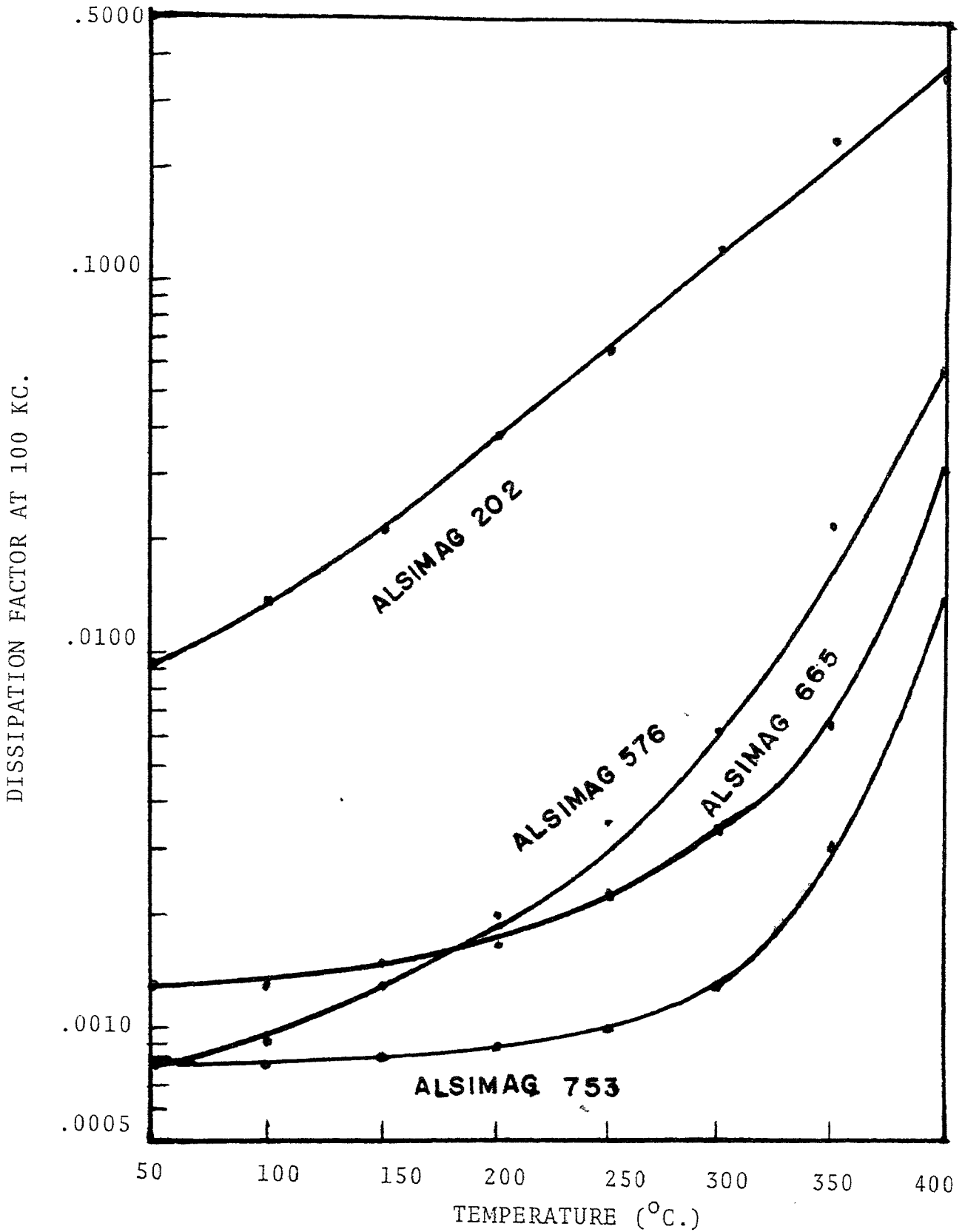


Figure 12. Observed dissipation factor, temperature relationships of commercial insulators from American Lava Co.

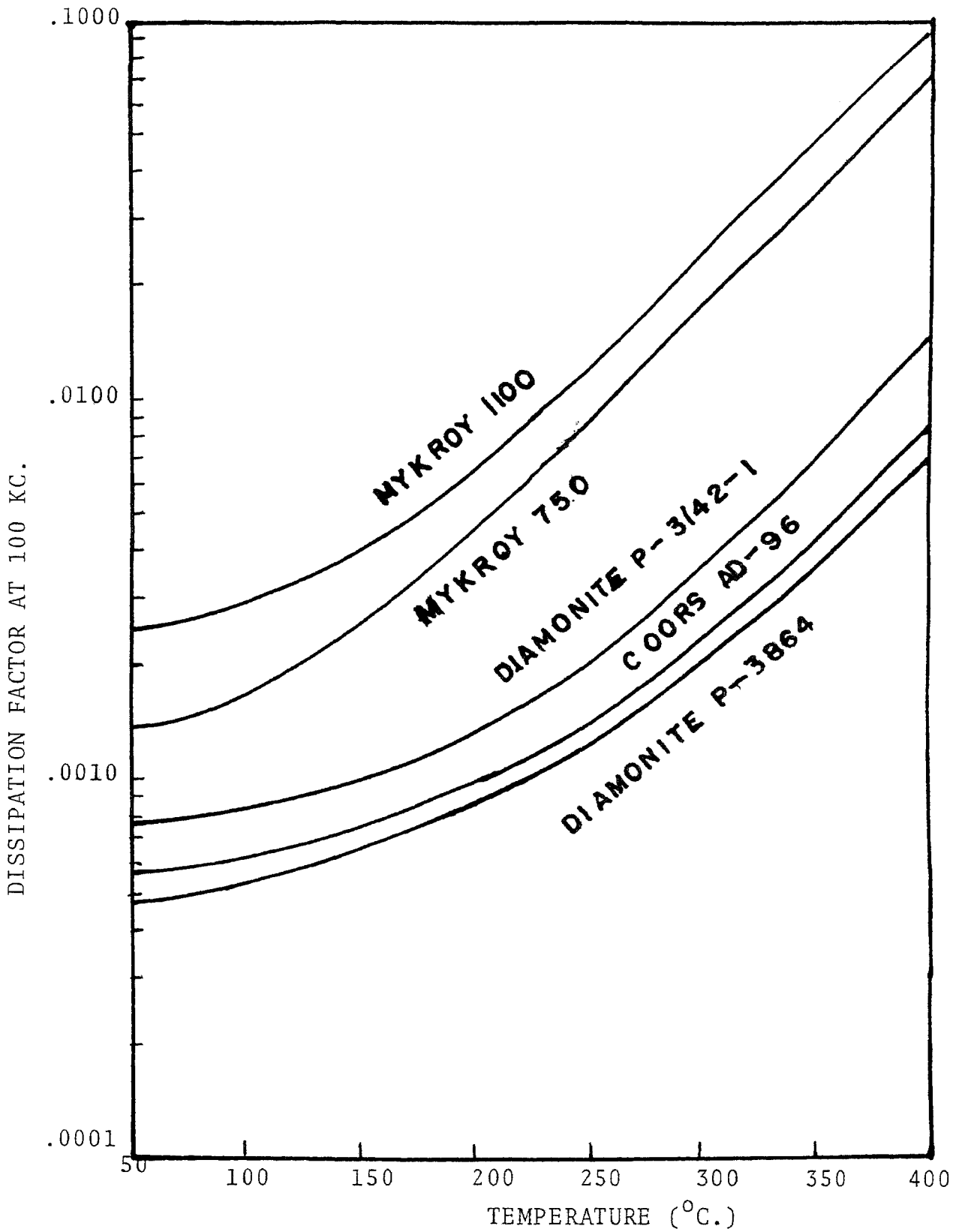


Figure 13. Observed dissipation factor, temperature relationships of Commercial insulators from Molecular Dielectrics Co., Diamonite Mfg. Co., and Coors Porcelain.

The percent of error connected with the General Radio 1610-B2 capacitance measuring assembly was negligible when compared to the precision of temperature measurement and control. A standardized chromel-alumel thermocouple was correct to 0.5°C . in the temperature range of this study. The thermal gradient inside the furnace chamber gave the greatest source of error. The maximum temperature difference in the furnace chamber was probably 10°C .

2. Dielectric Constant and Loss Changes During Nucleation and Growth of the Pseudocrystalline Phase

Two studies were conducted in an effort to detect changes in the dielectric and resistivity properties as nucleation and growth of the pseudocrystalline phase occurred. The first study involved following the changes in the dielectric properties of a glass disc heated at a rate of $2^{\circ}\text{C}/\text{min}$. to 680°C . The results of this study indicated a gradual increase in the dielectric properties up to 600°C . At 600°C ., a rapid drop in the dielectric constant from 27 to 22, and the dissipation factor from .9580 to .8460, occurred. The change in dielectric constant with temperature is reproduced in Figure 14.

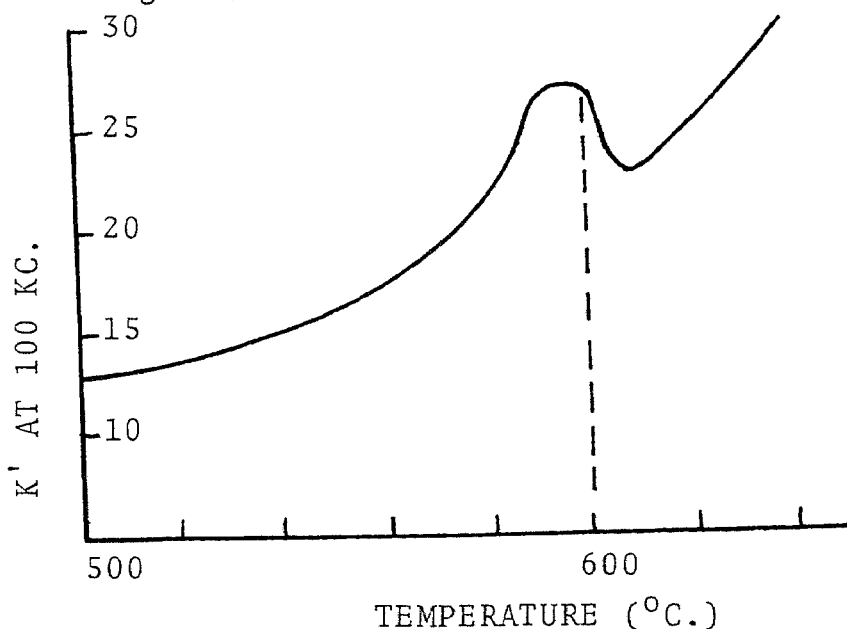


Figure 14. Observed dielectric constant, temperature relationships through glass-pseudocrystalline phase change.

An investigation of the resistivity properties gave similar results. There was a change in resistivity values from 1.2×10^7 ohm, cm. at 590°C ., to 1.2×10^5 ohm, cm. at 600°C ., then back to 1.2×10^7 ohm, cm. at 610°C .

3. Dielectric Properties of Heat-Treated Mica-Glass

The dielectric properties of the devitrified mica-glass at temperatures up to 400°C ., were measured at 100 kc. and are reported in Figures 15 and 16. The dielectric constant of the glass at 50°C . was 9.8, while the pseudocrystalline mica after heat treatment at 700°C . for 3 hours, had a value of 6.55. This striking change is related to an increase in the structural order of the specimens. At higher heat treatment temperatures of 800°C . and 900°C ., the dielectric constant decreased slightly, e.g., the dielectric constant observed after heat treatment at 900°C . for 3 hours was 5.75 at 50°C . Heat treatment temperatures above 900°C . produced no significant changes in the dielectric constant. Similarly, measurements of dissipation factor for samples heat-treated above 900°C . showed no significant differences. These highly devitrified materials had rather poor dissipation factors and are not suitable for commercial applications requiring grade L1 or better. However, the pseudocrystalline phase formed after 3 hours at 700°C . and the glass had dissipation and loss factors slightly above commercial Mykroy 1100, and L4 grade ceramic material.

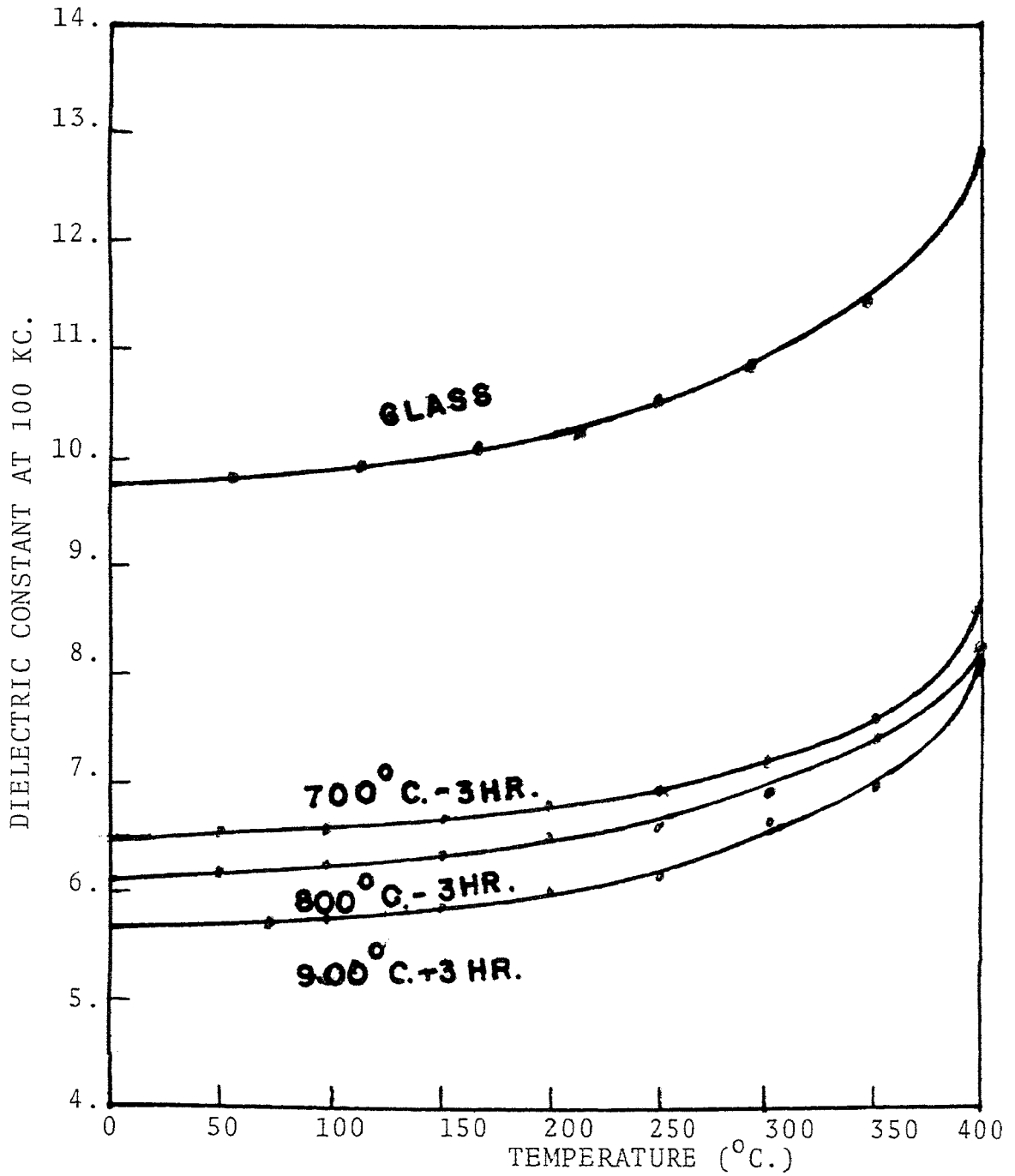


Figure 15. Observed dielectric constant, temperature relationships of tetrasilicic mica.

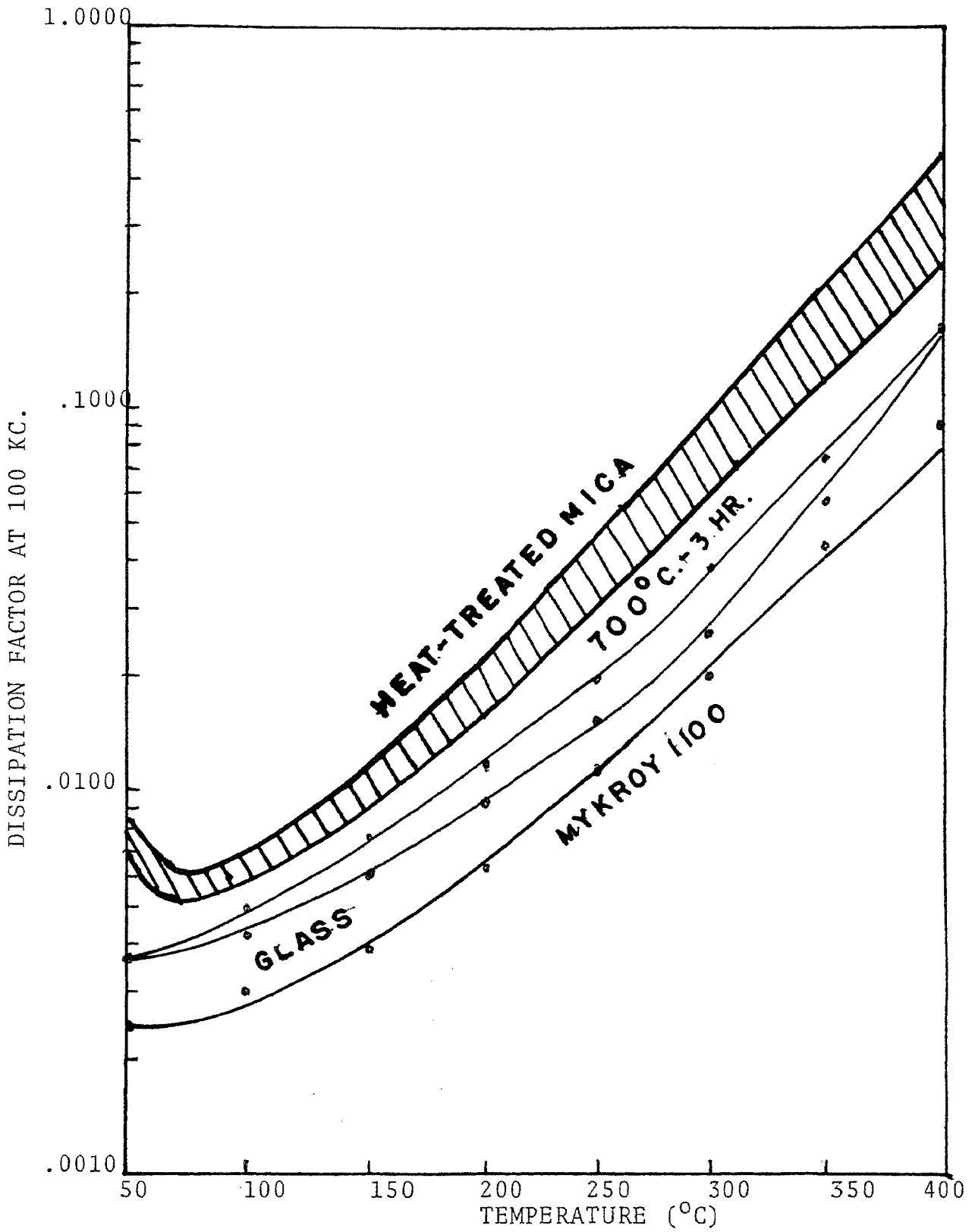


Figure 16. Observed dissipation factor, temperature relationships of tetrasilicic mica.

Resistivity measurements were made in an attempt to determine the cause of the poor dissipation values observed in the devitrified specimens. The resistivity of the glass and pseudocrystalline phase was higher than any of the heat-treated micas. A typical data set for crystallized mica obtained through heat treatment at 1150°C. for 6 days, is given in Table IX. These values resemble those obtained from other glass specimens heat-treated above 900°C.

TABLE IX.

Resistivity of Mica-Glass, Heat-Treated at 1150°C. for 6 Days

<u>Temperature (°C.)</u>	<u>Resistivity (ohm, cm.)</u>
25	2.0×10^{10}
50	5.1×10^{11}
100	5.1×10^{11}
150	2.2×10^{11}
200	4.5×10^{10}
250	3.6×10^9
300	2.6×10^8
350	2.9×10^7
400	7.3×10^5

V. DISCUSSION OF RESULTS

A. Structural Changes Deduced from X-Ray Diffraction Studies

A pseudocrystalline phase is formed after heat treatments at 700°C. for 3 hours. This phase is an intermediate one between the original glass and the mica phase. Growth of crystalline mica from the pseudocrystalline phase was detected after samples were heat-treated at 800°C. for 3 hours, and became more extensive at higher heat treatment temperatures. X-ray diffraction patterns of extremely fine-grained materials contain poorly defined diffraction peaks. Grain size of the mica in specimens receiving intermediate heat treatment was probably below 1000 Å. Therefore, the extent of crystallization occurring at the intermediate heat treatment temperatures could not be determined even semi-quantitatively. Nearly complete mica crystallization was definitely observed for the extended heat treatment at 1150°C. for 6 days. Decomposition products of the mica were not detected.

B. Structural Changes Deduced from Microstructure Changes

The pseudocrystalline phase produced after heat treatment at 700°C. for 3 hours visually resembles the original glass. The glass-mica, heat-treated at 1100°C. for 3 hours, exhibited a microstructure consisting of extremely small crystals. Higher devitrification temperatures caused the mica crystals to increase substantially in size, until after treatment at 1150°C. for 6 days, a final grain size of 100 microns in the longest dimension was attained.

C. Structural Changes Deduced from Physical Changes

Weight loss studies indicated that tetrasilicic mica is extremely stable at high temperatures e.g., the heat treatment at 1100°C. for 3 hours produced a .037% weight loss. Density values increased rapidly above 600°C. indicating increases in the amount of pseudocrystalline and/or mica

phase. The theoretical density of tetrasilicic mica was approached in specimens heat-treated at temperatures of 900°C. and 1000°C. This supports the supposition that the intermediate heat treatments produce a high degree of crystallinity. Imperfections in the microstructure were indicated by a decrease in the density at extreme heat treatments. These imperfections are probably voids created by oriented crystal growth.

D. Glass-Pseudocrystalline Phase Changes Deduced from Dielectric Studies

Dielectric property and resistivity measurements were utilized to follow a glass-pseudocrystalline phase transformation. At 600°C., a re-orientation of the glass structure occurred abruptly. The extent of the transformation was not determined quantitatively.

E. Commercial Applications of Heat-Treated Mica-Glass

The mica-glass and pseudocrystalline material were found to be slightly higher in dissipation and loss factor than a commercial L4 grade ceramic material. These materials should be useful dielectrics affording several advantages: (1) inexpensive forming methods, (2) uniformity of products, and (3) good dielectric properties at elevated temperatures. One special application could be in the production of thin films for use in capacitors and as a possible substitute for sheet mica.

The devitrified crystalline mica had a high dissipation factor and low resistivity which would make it unsuitable as a commercial insulator. These poor characteristics were believed to be a direct result of volatilization losses from the melt which induce non-stoichiometry in the mica. If these losses could be eliminated by different melting procedures, the devitrified material should have much better dielectric properties.

VI. SUMMARY AND CONCLUSIONS

A pseudocrystalline phase was found to develop as an intermediate phase prior to final devitrification of a tetrasilicic mica-glass. This pseudocrystalline intermediate phase is formed at temperatures above 600°C. and possesses some ordering of the crystalline state. Results from this and other parallel property investigations now being conducted indicate an intermediate phase change which is abrupt and results in an extensive change of the glass to the pseudocrystalline phase. The crystalline mica grows from the pseudocrystalline phase and may attain complete development after intermediate heat treatments at 900°C. and 1000°C. for 3 hours. A stoichiometric mica-glass should produce a 100% yield of tetrasilicic mica. Extended high temperature heat treatments promote grain growth, e.g., heat treatments at 1150°C. for 6 days produced particles 100 microns in the longest dimension. During the process of grain growth, reorientation of the particles apparently causes void imperfection to develop.

During the initial stages of mica formation from the pseudocrystalline phase, density and shrinkage increased sharply. The theoretical density of tetrasilicic mica is 2.835 and was closely approached after heat treatments at 900°C. and 1000°C. Higher temperature heat treatments produced a decrease in the densities and an expansion of the specimen.

The following conclusions with regard to useable dielectric properties of materials are made from the results of this study:

1. The mica-glass and the pseudocrystalline mica are nearly comparable in loss factor to several commercial grade L4 ceramics, and should be useful in many dielectric applications where these specifications must be met.

2. The dissipation factor for the heat-treated crystalline mica is higher than acceptable for good insulating materials. This was directly attributable to a low d-c resistivity, very probably a result of non-stoichiometry in the starting glass composition. Crystal orientation and excessive grain growth at the highest temperatures of heat treatment further deteriorate the dielectric loss properties.

VII. SUGGESTIONS FOR FUTURE WORK

Some recommendations for future studies follow:

1. Better melting procedures should be developed to reduce volatilization and thereby correct the apparent non-stoichiometry. These procedures might utilize tightly sealed platinum containers or internal resistance melting.
2. A thermogravimetric study in conjunction with weight loss-composition studies is necessary to accurately determine the degree of volatilization.
3. Electron micrographs could be utilized to determine the degree of crystallization after the intermediate heat treatments at 900°C . and 1000°C .
4. Differential thermal analysis, refractive index, and thermal expansion measurements might also be used to determine the extent of phase transformations.

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