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287 174

INORGANIC DIELECTRICS RESEARCH

PROGRESS REPORT NO. 1

Contract No. DA-36-039-sc-39141

November 1, 1961 to February 1, 1962

Signal Corps Research Program
File No. 01007-PM-62-93-93

N. J. CERAMIC RESEARCH STATION
Rutgers, The State University
John H. Koenig, Director

Investigators (Full Time)

E. J. Smoke
C. J. Phillips
E. L. Kastenbein
D. R. Ulrich
R. C. Pitetti
J. R. Smyth
C. Breen

Assistants (Part Time)

J. Thomson
W. Hoagland
J. Rubin
J. Wasylyk
J. Buckmelter



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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACTS.....	i
Part I - Low Loss Microwave Ceramic Dielectrics.....	i
Part II - Transparent Polycrystalline Ceramics.....	i
Part III - Hot Extrusion.....	ii
PART I - LOW LOSS MICROWAVE CERAMIC DIELECTRICS.....	1
Introduction.....	1
I. Hot-Pressing.....	2
II. Investigation of Crystalline Phases Present.....	9
A. Introduction.....	9
B. Literature Research.....	10
C. Experimental Work.....	11
D. Results.....	16
III. Summary.....	18
Future Work.....	18
PART II - TRANSPARENT POLYCRYSTALLINE CERAMICS.....	20
Introduction.....	20
Experimental Work.....	21
Results.....	23
Future Work.....	26
PART III - HOT EXTRUSION.....	28
Introduction.....	28
Equipment.....	29
Experimental Work.....	31
Discussion of Results.....	32
Conclusions.....	33
Future Work.....	33

Part I

LOW LOSS MICROWAVE CERAMIC DIELECTRICS

Abstract

Three compositions in the $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system were hot-pressed and the electrical properties measured at several frequencies and temperatures. A study was made of the crystalline phases appearing in a number of compositions within the system. Two lanthanum silicate compounds, lanthanum aluminate and mullite were found in the various compositions. Attempts to form each lanthanum silicate compound by itself are being made in order to evaluate their electrical properties. This information will be used in attempting to tailor bodies to meet the specific requirements of this project.

Part II

TRANSPARENT POLYCRYSTALLINE CERAMICS

Abstract

Specimens of pure alumina were pressed and sintered using a two-fire procedure. For the initial firing, one set of specimens was fired in air and one set was fired in argon. The second firing of both sets was performed in argon. Bulk densities of the two sets of specimens were measured and compared. Specimens which were initially fired in air were less dense than those fired wholly in argon.

Part III
HOT EXTRUSION

Abstract

The hot extrusion apparatus is described and its operation explained. The results of three extrusion attempts are described.

Progress Report - Part I
LOW LOSS MICROWAVE CERAMIC DIELECTRICS

Introduction

The object of this problem is to develop low loss insulation with a dielectric constant of 15 and a power factor not to exceed 0.0004 at microwave frequencies and at temperatures between -50 and +300°F. The dielectric constant is above that of the recognized range for insulation.

In earlier work, two lanthanum alumino-silicate compositions exhibited these desired values as determined at 1 megacycle and room temperature. The compositions were LAS-2 (1.96 weight percent of Al_2O_3) and LAS-5 (4.76 weight percent of Al_2O_3)¹. Both of these compositions were fired conventionally after an involved preprocessing procedure. The processing of these compositions consisted of drying the La_2O_3 for one day prior to batching, wet ball milling the compositions for one day, calcining the compositions three times, screening the material between each calcining operation, pressing the desired pieces, and then slow firing the pieces to vitrification. This processing of the compositions took about one week to complete.

1. Inorganic Dielectrics Research, Progress Report No. 1, March 1, 1960

Rutgers, The State University
Signal Corps Contract No. DA-36-039-sc-89141

Efforts were made to reduce the processing time by two methods: by a high temperature pre-firing, and by a single calcination in place of the three calcinations used previously. Both of these attempts resulted in materials exhibiting critically short firing ranges, porous bodies and, consequently, unreproducible and unreliable results. For this reason, hot-pressing the compositions was tried and resulted in the production of dense bodies of approximately the desired properties within at least a portion of the frequency and temperature range.

This report deals with the results obtained by hot-pressing and with analysis of the crystalline phases formed in fired pieces of a number of compositions in the ternary system.

I. Hot-Pressing

Since firing of these bodies by conventional means was not successful without calcining three times prior to the final firing, it was decided to try fabrication by hot-pressing. This technique produced bodies that had 0.002 moisture absorption and electrical properties that were near the desired values.

Three bodies were hot-pressed: K15, K15+1 and K15+3. The compositions of these bodies in weight and mol percentage are given in Table I.

Table I

	La_2O_3		SiO_2		Al_2O_3	
	<u>wt. %</u>	<u>Mol. %</u>	<u>wt. %</u>	<u>Mol. %</u>	<u>wt. %</u>	<u>Mol. %</u>
K15	61.56	26.4	33.14	65.0	5.30	8.6
K15+1	61.32	26.3	32.93	64.5	5.75	9.2
K15+3	60.67	25.4	32.68	64.1	6.65	10.5

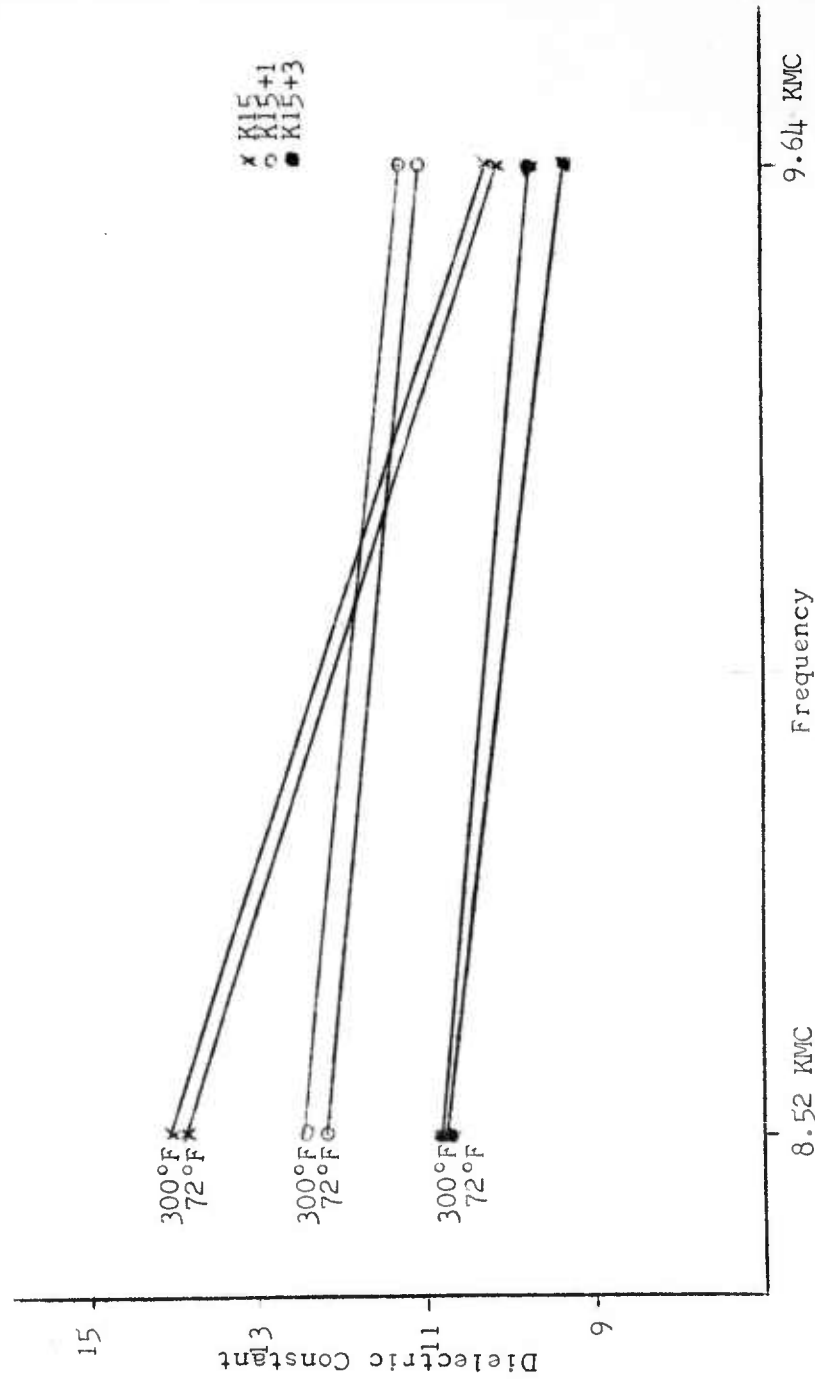
The La_2O_3 is extremely hygroscopic and was treated for 20 hours at 1400°F to drive out the water. The materials were then weighed, dry-mixed for two hours, and wet ball-milled for twenty hours. This material was then dried and passed through a 100 mesh screen.

Hot-pressing of the screened material was performed in 1" ID x 3" OD x 3" high graphite dies which had been lined with 0.005" sheet molybdenum to minimize carbon migration. The dielectric constant of composition K15 decreased the greatest amount with an increase in frequency between 8.52 and 9.64 KMC. Graphic presentations of the change of the dielectric constant with frequency and temperature are given in Figures 1 and 2 on pages 4 and 5 respectively. The graphs indicate that the dielectric constant is not very temperature sensitive at these frequencies, but that there are large changes in the dielectric constant with changes in the frequency.

Table II

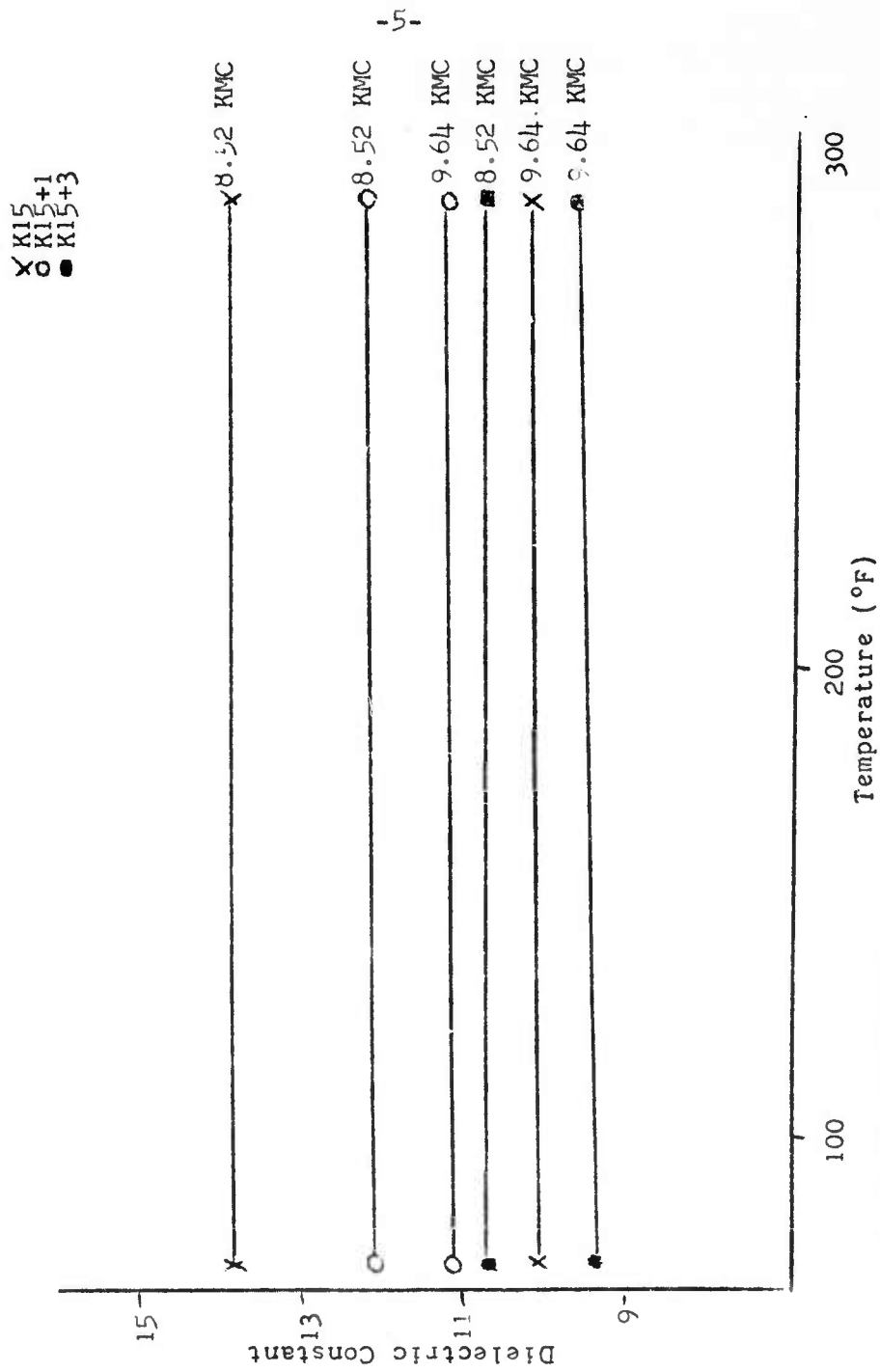
<u>Body</u>	<u>Bulk Density (g/cm³)</u>	<u>Frequency (KMC)</u>	<u>Temp. °F</u>	<u>Dielectric Constant</u>
K15	4.18	8.52	72	13.9
		9.64	72	10.15
		8.52	300	14.0
		9.64	300	10.35
K15+1	4.20	8.52	72	12.2
		9.64	72	11.1
		8.52	300	12.45
		9.64	300	11.3
K15+3	4.11	8.52	72	10.8
		9.64	72	9.48
		8.52	300	10.85
		9.64	300	9.84

Figure 1
 VARIANCE OF DIELECTRIC CONSTANT AT HIGH FREQUENCIES



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Figure 2
 VARIANCE OF DIELECTRIC CONSTANT WITH TEMPERATURE



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After hot-pressing the specimens were machined to fit the waveguide in the dielectrometer (0.250" x 0.396" x 0.890"). When this size specimen was placed in the waveguide of the dielectrometer, it was found that the length dimension (.250") was too small to determine $\tan \delta$ accurately. $\tan \delta$ is given by:

$$\tan \delta = \frac{\Delta X}{d} F(K, d, \lambda)$$

where $F(K, d, \lambda)$ depends on dielectric constant of the specimen, specimen length, and wavelength in the waveguide. However, the effect of d , the sample length, on $F(K, d, \lambda)$ is minor compared to its effect on $\frac{\Delta X}{d}$. The ΔX , then, produced by the specimen, is approximately proportional to d and $\tan \delta$. Therefore, for low loss specimens, d must be made large enough to produce a ΔX which is much larger than the ΔX caused by waveguide losses.

The dielectrometer specimens were also used to obtain approximate measurements of the dielectric constant and power factor at 1 megacycle and room temperature using the Q-meter. The size and shape of the samples did not lend themselves to direct measurement by the Q-meter so the data obtained had to be corrected for edge effects. There were no calculated corrections for the size sample used so that the values given in Table III are only close approximations. The plus sign given next to the dielectric constant indicates the given value is somewhat smaller than the actual value would be if the sample was a size where

there would be no "edge effects." The minus sign, next to the power factor indicates that the actual value is smaller than the value given.

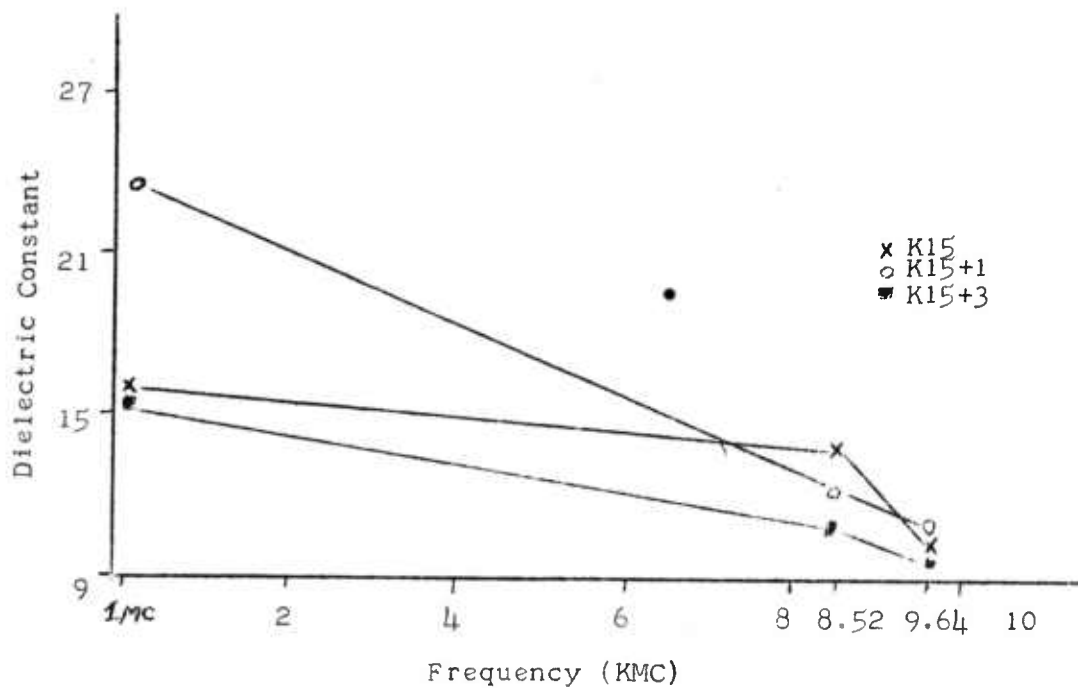
Table III

<u>Body</u>	<u>K</u>	<u>P. F.</u>	<u>Bulk Density (g/cm³)</u>
K15	+16.0	-.00108	4.18
K15+1	+23.8	-.00058	4.20
K15+3	+15.4	-.00084	4.11

If the values for the dielectric constant calculated at 1 megacycle and room temperature are considered with the higher frequency values at 72°F, then much more information can be obtained. With body K15, there is a sharp decrease of the dielectric constant in the higher frequency regions. With body K15+3, there is also a greater decrease at the higher frequency but not quite as great as body K15. Composition K15+1 appears to have a more linear decrease in the dielectric constant over the entire frequency range investigated. A graph of this information appears in Figure 3 on page 8. New specimens are being hot-pressed for more precise electrical measurements.

It was apparent that a small amount of carbon or molybdenum had migrated into all the hot-pressed specimens. In all probability, this migration increased the power factor of these bodies. An attempt will be made to hot-press these bodies in ceramic dies to eliminate this contamination.

Figure 3
VARIANCE OF DIELECTRIC CONSTANT WITH FREQUENCY
AT ROOM TEMPERATURE



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The application of the hot-pressing technique has produced results which approach the requirements of the project. Furthermore, if the results of the dielectric properties at 1 megacycle can be held reliable, then we can see that there is an increase in the dielectric constant with increasing alumina percentage up to 9.2 mol percent and then there is a decrease in the dielectric constant with greater percentages. With the power factor the reverse is true. The power factor is high at 8.6 mol percent of alumina, low at 9.2 mol percent and then a slight increase at 10.5 mol percent. These results can be made reliable only through further experimentation with these compositions.

II. Investigation of Crystalline Phases Present

A. Introduction

Since compositions within the $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system exhibit promise of producing bodies satisfying the technical requirements desired in this phase of work, a study of the crystalline phases occurring was deemed desirable. If these crystalline phases can be identified, attempts can be made to produce bodies containing a maximum quantity of each given phase. Evaluation of the properties of these phases should be extremely useful in tailoring bodies to meet the technical requirements of the contract.

B. Literature Research

The preliminary research done for this investigation was the accumulation of information on the various binary compounds. The binary compound of alumina and silica is mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). This is a well explored binary and thus there is sufficient information dealing with the identification of the compound.

Two compounds exist in the lanthanum oxide-alumina system: $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ and $\text{La}_2\text{O}_3 \cdot 12\text{Al}_2\text{O}_3$. The 1:1 compound has a perovskite-type structure and is stable from room temperature to its melting point at 2130°C . The X-ray powder diffraction pattern has been given in earlier reports. The 1:12 compound is similar in structure to $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ and is stable to 1920°C , where it melts congruently².

A recent thesis by Warshaw³ has shown that there are two compounds in the lanthana silicate binary: $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$. The compound $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ is typical of the pyrosilicates of the larger rare earths, comprising La, Ce, Pr, Nd, Sm and Eu. There is a high and low temperature form of $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ (β and α respectively). The orthosilicate ($\text{La}_2\text{O}_3 \cdot \text{SiO}_2$) melts congruently at 1980°C while the 1:2 compounds melts incongruently at 1760°C forming the 1:1 compound and a liquid. As in the case of $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$, lanthanum orthosilicate also has two polymorphs

2. Warshaw, Israel, Phase Equilibrium and Crystal Chemical Relations in Rare Earth Systems, Department of Chemistry, Penn State U.

3. *ibid.*

with the transition temperature being 1275°C.

The phase equilibrium diagram given by Warshaw, Figure 4 on page 12, bears little resemblance to that published by Toropov and Bondar⁴ which was given in earlier reports. Instead of finding two compounds, they found only a 2:3 compound. This difference would completely alter the phase equilibrium relationships in the remainder of the system. Only the compounds reported by Warshaw have been identified in the present study.

C. Experimental Work

A number of compositions were prepared to investigate the compound formation occurring in the ternary system. The lanthanum oxide was dried at 1400°F for 20 hours before the batches were weighed. The compositions were then dry ball-milled for seven hours. One inch discs were pressed and fired with no soak. Vitrification and compound formation was obtained using draw trials method. The fired specimens were crushed to pass through a 200 mesh screen and then X-rayed.

The compositions used in this study are given in Table IV on page 13 and their locations are shown in the two ternary diagrams, Figures 5 and 6 on pages 14 and 15. Indicated also in these

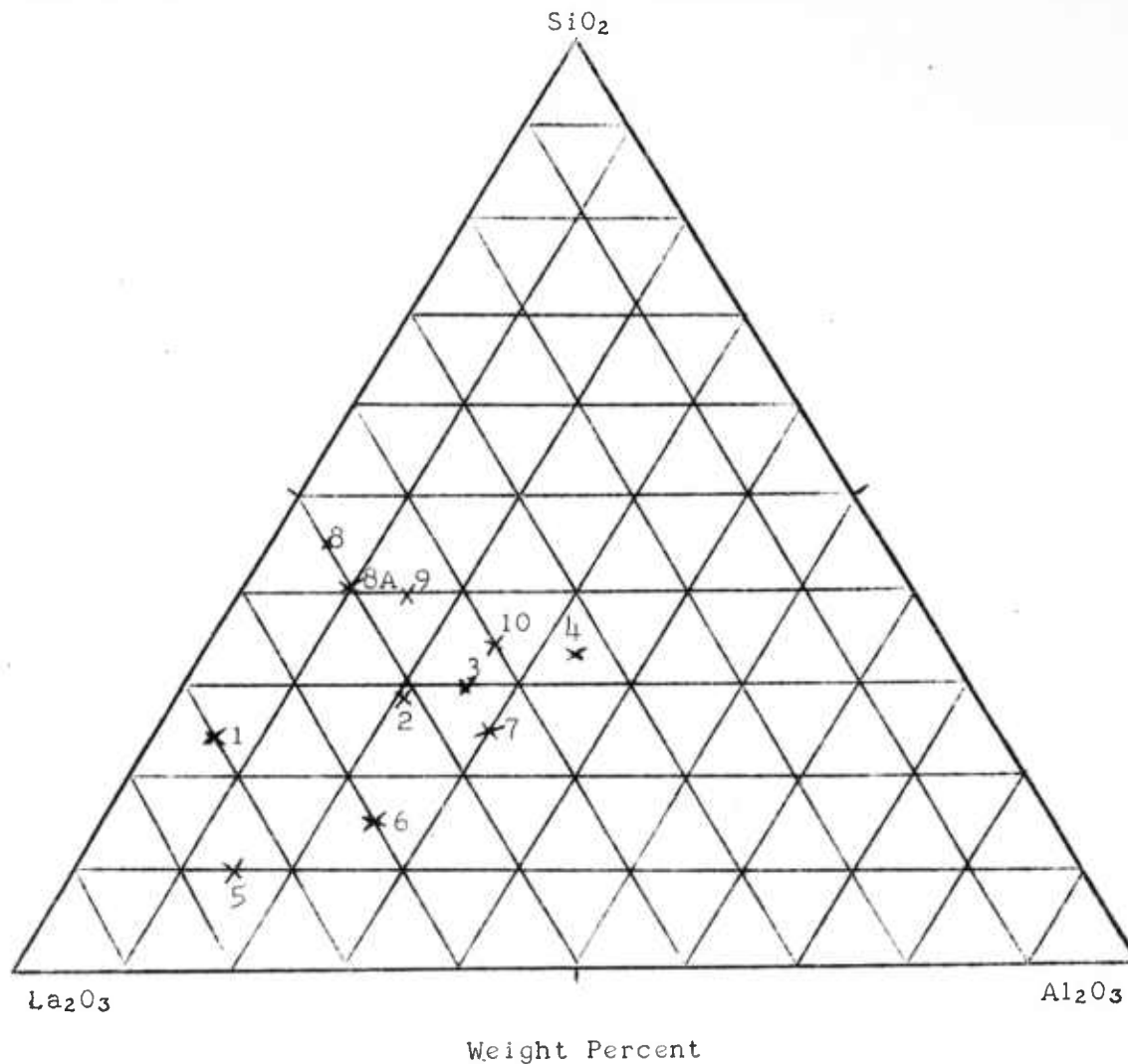
4. Warshaw, Israel.

Table IV

<u>Compound</u>	<u>La₂O₃</u>		<u>SiO₂</u>		<u>Al₂O₃</u>	
	<u>Wt. %</u>	<u>Mol. %</u>	<u>Wt. %</u>	<u>Mol. %</u>	<u>Wt. %</u>	<u>Mol. %</u>
1	70	35.6	24	56.0	6	8.4
2	55	24.2	28	55.6	17	20.2
3	45	17.8	30	54.9	25	27.3
4	33.3	11.3	33.3	55.4	33.3	33.3
5	75	46.2	10	28.0	15	25.8
6	60	29.8	15	35.1	25	35.1
7	45	18.5	25	47.4	30	34.2
8	50	18.4	45	76.5	5	5.1
8A	50	16.1	40	69.9	10	14.0
9	45	16.5	40	68.1	15	15.4
10	40	14.8	35	59.5	25	25.8

Figure 5

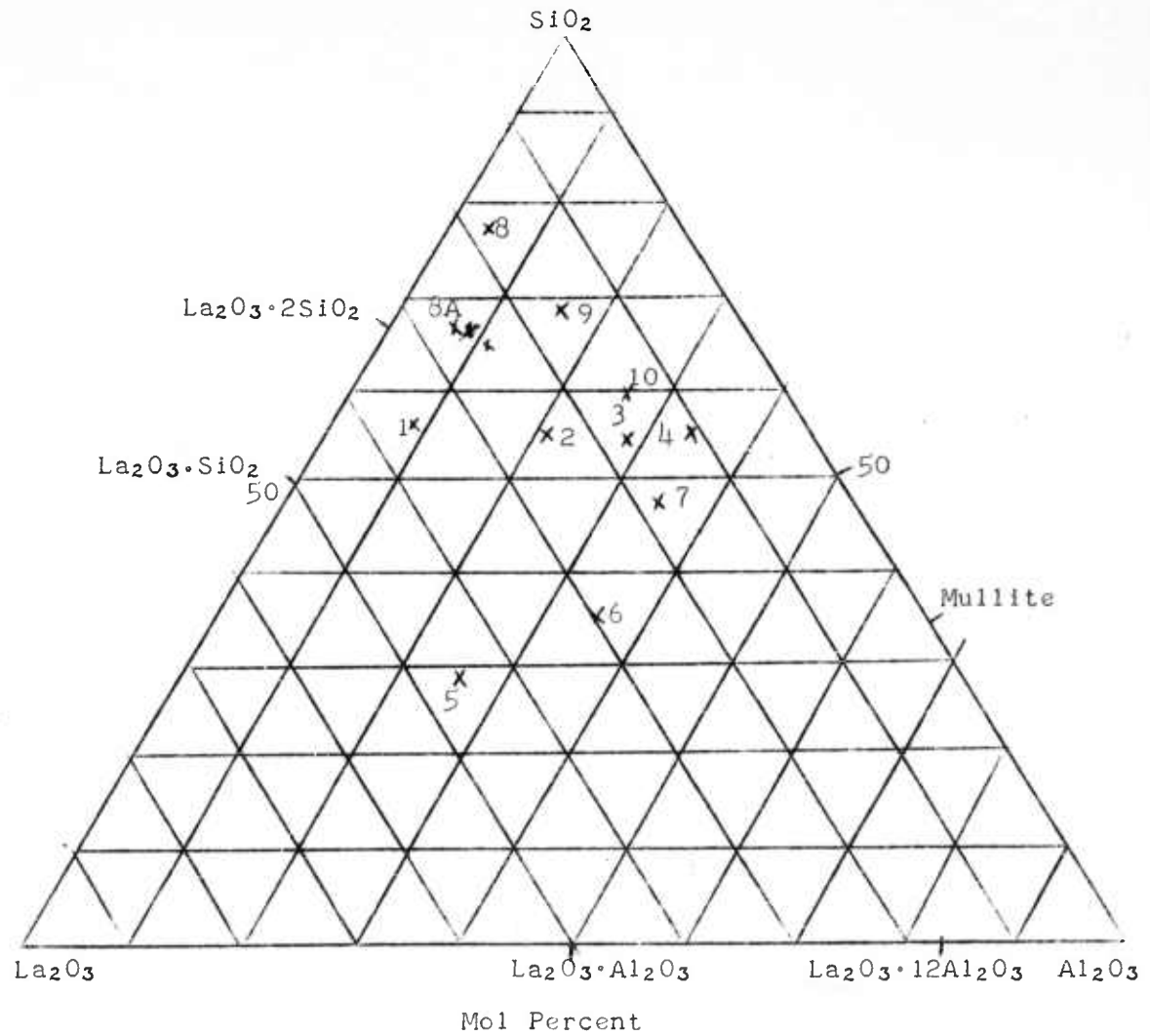
LOCATIONS OF COMPOSITIONS IN WEIGHT PERCENTAGES



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Figure 6

LOCATIONS OF COMPOSITIONS IN MOL PERCENTAGES



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diagrams are the locations of the compositions that had been hot-pressed. Comparing the two diagrams (one in weight percent and the other in mol percent), it can be seen that the compositions fall in the high lanthana area when using a weight percent diagram but they fall in the low lanthana part of the ternary when using mol percent. It has been postulated that if a ternary compound would exist it would be in the low mole percent lanthana region⁵.

The results of the X-ray analysis of this work indicated that there were no ternary compounds in the area evaluated. Two lanthanum silicate compounds, lanthanum aluminate, mullite and the three starting oxides in various forms were found in different compositions. The compounds found in the different compositions are shown in Table V on page 17.

D. Results

As can be seen from Table V, there appears to be no ternary compound. Furthermore, $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ appears to have formed in most of the compositions, but $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ appeared in only a small number of compositions.

It will be noted that all three of the compositions (K15, K15+1, and K15+3) on which electrical properties have been obtained contain mullite, $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ and $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$. The electrical properties of all of these phases except $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ are known. Therefore, it is important to attempt to produce

5. Warshaw, Israel, *ibid.*

Table V

Crystalline Phases

Body	Mullite	$\frac{\text{La}_2\text{O}_3}{\text{Al}_2\text{O}_3}$	$\frac{1\text{La}_2\text{O}_3}{12\text{Al}_2\text{O}_3}$	$\frac{1\text{La}_2\text{O}_3}{2\text{SiO}_2}$	$\frac{1\text{La}_2\text{O}_3}{2\text{SiO}_2}$	$\frac{\text{La}_2\text{O}_3}{\text{SiO}_2}$	La_2O_3	Al_2O_3	Crist.
1	X	X		X		X		X	α
2	X	X		X		X		X	
3	X	X		X		X		X	β
4	X	X		X		X(?)		X	
5		X				X			
6		X				X			
7	X	X		X		X		X	α
8	X			X					α
8A	X			X					α
9				X				X	α
10				X				X	α
K15	X	X		X		X			α
K15+1	X	X		X		X			α
K15+3	X	X		X		X			α

X = indicates crystalline phase present

the latter compound and determine its electrical properties. If the properties of both the 1:1 and 1:2 lanthana-silica compounds can be determined, this information should be most helpful in preparing bodies to meet the desired technical requirements.

III. Summary

The dielectric properties of K15, K15+1, and K15+3 prepared by hot-pressing at least approach the desired values. It appears that these compositions are only slightly temperature sensitive at the higher frequencies but are quite frequency sensitive. The highest dielectric constant recorded was found using 9.2 mol percent of Al_2O_3 and the lowest $\tan \delta$ was also recorded at this percentage. Any increase in the alumina content decreased the dielectric constant and increased the $\tan \delta$.

The compositional study of the ternary system revealed that $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ was the dominant compound formed in the areas studied. Also formed within the ternary were $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$, mullite, LaAlO_3 . All of the compositions evaluated exhibit short firing ranges which indicated that vitrified bodies will be extremely difficult to form using the conventional firing techniques.

Future Work

1. Hot-press new specimens K15, K15+1 and K15+3 to evaluate $\tan \delta$ at microwave frequency.
2. Hot-press $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ to determine the dielectric properties.

3. Hot-press ternary compositions and evaluate their dielectric properties.

4. Use information obtained in 2" above to prepare compositions believed to have the most promise of fulfilling the technical requirements of this project.

Progress Report - Part II
TRANSPARENT POLYCRYSTALLINE CERAMICS

Introduction

The objective of this program is to produce a transparent or highly translucent, polycrystalline, single-oxide dielectric of very high density and essentially void free. In addition to transparency, the material should also possess the following properties: a low dielectric constant, low power factor, dielectric strength of 400 volts/mil for 1/4" specimens, and high mechanical strength.

As has been stated in previous reports, the preliminary work in this investigation has been on alumina. Alumina was chosen for this work since transparent, polycrystalline specimens of it have been produced by other investigators¹. Furthermore, a considerable amount of information on the sintering of alumina is found in the literature. Therefore, in starting with a study of alumina, a material is being used which is not only known to be capable of producing transparent, polycrystalline specimens, but about which a maximum number of the conditions required for the production of transparent specimens are known. Close examination of the

1. Australian Patent, "Improvements in or Relating to Transparent Alumina."

Rutgers, The State University
Signal Corps Contract No. DA-36-039-sc-89141

parameters involved in production of transparent, polycrystalline alumina should be extremely valuable in future work on other oxides. The use of isotropic crystalline materials should allow production of specimens having a higher degree of transparency than alumina since alumina is anisotropic.

Two methods of maturation are planned: sintering and hot-pressing. However, as of this date, only the former technique has been studied. The transparent alumina previously mentioned was fabricated by sintering. The aluminum oxide used was of high purity, having only 0.3% of magnesia. Alpha alumina was the only crystalline phase present. The crystal size after sintering ranged from 15 to 65 microns.

In the present investigation, the procedure outlined in the Australian patent was followed closely, with certain modifications. One of these was that a different gaseous environment was used.

Experimental Work

The apparatus used for sintering has been described in the previous report. A diagram of the sintering furnace appeared in Figure 1 on page 38 of that report. It is essentially a water-cooled, induction furnace, containing an induction coil, and a molybdenum susceptor, surrounded by a quartz tube and insulated with zirconia sand as loose fill. The sample rests on a small piece of molybdenum on a zirconia setter.

The procedure as described in the above-mentioned patent calls for two separate firings: First, a firing at a temperature from 1650° to 1750°C for a period of from 50 to 300 minutes, to eliminate most of the voids and gas containing pores; secondly a firing at a temperature of from 1850° to 1950°C, for a period of not less than fifteen minutes. The first firing may be done in any atmosphere, while the body is always subjected to an atmosphere of hydrogen in the second firing.

In the present program, argon was substituted for the hydrogen. There are several reasons why this was done. First, it was felt that hydrogen could not be safely used with the present set-up. Further, a literature review failed to reveal any previous work utilizing an argon atmosphere. Hence, much new information could be obtained in this area. Finally, the argon serves to protect the molybdenum susceptor from oxidation.

Samples of pure alumina (99.9+%) in a colloidal form having a maximum particle size of 0.3 microns, were pressed into compacts 1/2 inch in diameter and 1/8 inch thick. Half were fired in a gas-fired kiln in a slightly oxidizing atmosphere for one hour at 1700°C. The other half were fired in argon at the same temperature and for the same length of time. All samples were then subjected to a second firing to 1900°C in an atmosphere of argon and held for periods of 15, 60, and 300 minutes respectively.

Results

Densities obtained with the samples of fired alumina are listed in Table I on page 24. The results are shown graphically in Figure 1. As can be seen, the densities obtained were quite low, and the specimens were not transparent.

The samples were all coated with a thin silvery metallic layer, probably from condensation of vaporized molybdenum. However, the films were very thin and were easily removed by grinding. The coatings did not appear to have diffused into the specimens. Hence, the lack of transparency was undoubtedly due, not to the contamination of the metal, but to the large percentage of voids present in the fired piece. An examination of the table reveals that the most dense sample obtained still contained voids to the extent of nearly 5%. In order to obtain transparency, less than 0.5% of voids is believed to be necessary.

It is postulated that the presence of these voids is due to uninhibited grain growth. If grain growth is too rapid, gaseous inclusions become entrapped within the crystals rather than at crystal boundaries. Pores within individual crystals have been found to very difficult to remove. Grain growth must be slowed down enough to permit diffusion of interstitial pores from the body. In order to inhibit this growth and to allow it to proceed at a rate slow enough to permit elimination of the voids, a small amount of some other material must be added. The next series of samples is therefore being made up with 0.7% of magnesia added to the alumina.

Table I
DENSITIES AND MOISTURE ABSORPTIONS OF SINTERED ALUMINA

A. Samples initially fired in air (1700°C)

<u>Additional Fire, 1900°C</u>	<u>Bulk Density</u>	<u>% True Density</u>	<u>Moisture Absorption</u>
0 min.	3.67	92.0	0.88
15 "	3.71	93.0	0.11
60 "	3.75	94.0	0.02
300 "	3.76	94.5	0.02

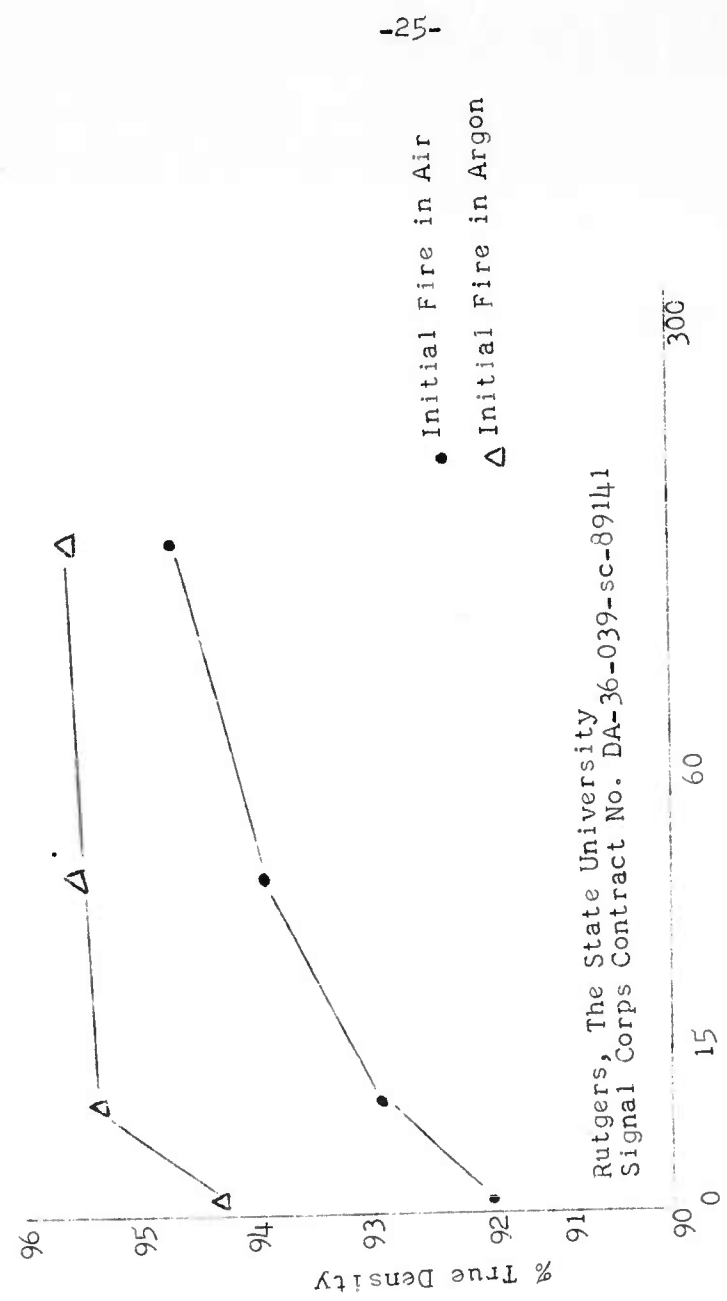
B. Samples initially fired in argon (1700°C)

<u>Additional Fire, 1900°C</u>	<u>Bulk Density</u>	<u>% True Density</u>	<u>Moisture Absorption</u>
0 min.	3.77	94.5	0.39
15 "	3.82	95.5	0.06
60 "	3.82	95.5	0.02
300 "	3.82	95.5	0.02

(Theoretical density of α -alumina = 3.987)

Figure 1

BULK DENSITY OF SINTERED ALUMINA



Rutgers, The State University
Signal Corps Contract No. DA-36-039-sc-89141

Additional Sintering Time (min.)
Second Fire (1900°)

(Theoretical Density of α -alumina = 3.987)

It is also planned to fire in an atmosphere containing aluminum vapor. The purpose of the aluminum is to create structural defects. The increase of vacancies in the lattice should increase the sintering rate by enhancing the diffusion of pores through the structure. It is hoped to thus be able to eliminate the voids and produce theoretically dense bodies.

Table I reveals that those samples fired initially in argon, have higher densities than those which were given an initial fire in air. The significance of this is open to question at this time since only a small number of specimens have been tested. Polished sections of the specimens are now being made for microscopic examination. This will permit determination of grain size and amount, size, and location of pores which will be necessary in evaluating the effects of different sintering conditions.

Future Work

1. Polished sections will be made of sintered specimens.
2. Specimens will be pressed with alumina containing a small amount of MgO to inhibit grain growth, and will be fired in the manner described above.
3. The furnace set-up will be altered slightly to permit firing in an atmosphere containing aluminum metal vapor.
4. A furnace is currently being built which will permit firing in a vacuum or in various atmospheres. As soon as it is finished, alumina will be subjected to firing in an atmosphere of hydrogen.

5. Samples have previously been prepared by hot-pressing. However, they were contaminated from the graphite die. Future samples will be prepared by hot-pressing in ceramic dies.

6. When work is completed on alumina, investigation of cubic phases, particularly magnesia, will begin. The literature reveals that MgO can be fabricated to theoretical density by hot pressing. However, no mention is made of transparency.

Progress Report - Part III

HOT EXTRUSION

Introduction

Hot extrusion of certain ceramic materials is foreseen as a method of producing materials having the desirable properties of hot pressed materials but being a more economical production method. For instance, earlier work has shown that barium titanate can be hot extruded and that the extruded material possesses qualities similar to that produced by hot pressing. The previous work was only preliminary and, although it did provide encouragement that hot extrusion of ceramic materials is feasible, it also demonstrated that there are a number of problems which will have to be solved before truly successful hot extrusion of these materials can be accomplished. Briefly the problems are:

1. Lubrication of the material being extruded so that it will flow readily through the die.
2. Maintaining the material being extruded at the proper temperature during the time necessary for extrusion.
3. Controlling the cooling rate of the extruded material to eliminate failure due to thermal shock.

The extrusion of materials such as glasses is relatively simple since these materials exhibit a gradual softening over

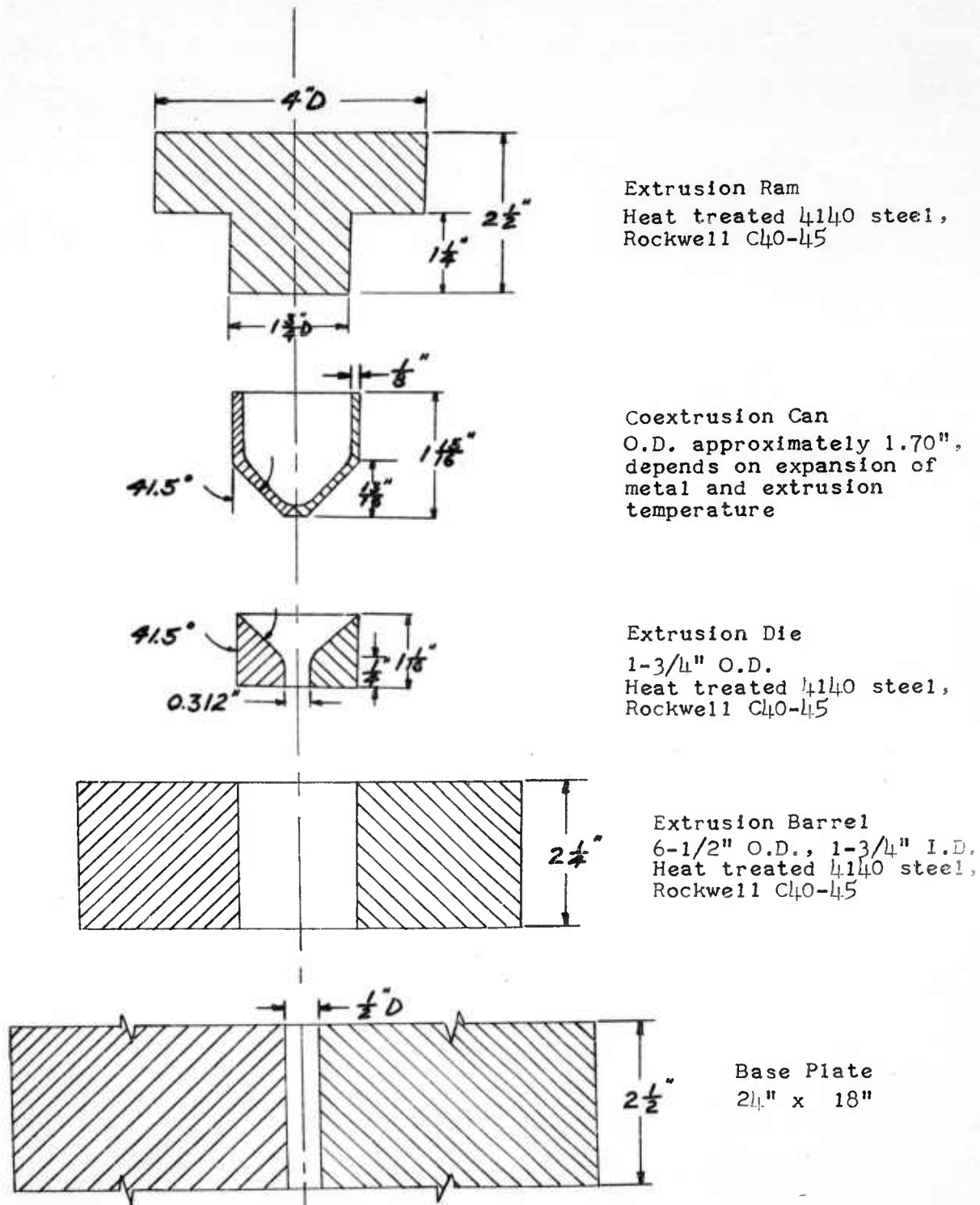
a reasonably large temperature range and essentially true viscous flow. However, crystalline ceramic materials have distinct melting points, going from a solid material exhibiting only a small degree of flow to rather fluid melts, over a very narrow temperature range. Although it is known to be possible to slowly extrude crystalline ceramics at some temperature below their melting point, rapid extrusion at such temperatures is not believed to be possible without lubrication. One means of providing lubrication without dilution of the desired crystalline phase is by coextrusion of a metal or glass cladding around the crystalline material. The coextrusion of a metal was used in the previous work on barium titanate and has also been successfully used by Nuclear Metals, Inc. for the hot extrusion of UO_2 ¹. The coextrusion of metal cladding around the ceramic is the method of lubrication being used in the present study.

Equipment

An exploded view of the extrusion assembly being used presently is shown in Figure 1. The press used is an electrically operated, hydraulic, 150 ton, constant pressure Dake Press, Model No. 21-150. The ram speed of this press is approximately 17 inches per minute.

1. J. G. Hunt and P. Loewenstein, "The Fabrication of Clad Massive UO_2 Fuel Elements by Coextrusion," Fourth Quarterly Report, Contract No. AT(30-1)-1565, Nuclear Metals, Inc., Concord, Mass., June 6, 1960.

Figure 1
Exploded Cross Section of
Hot Extrusion Assembly



In use, the extrusion barrel with the die in place rests upon the base plate. It is positioned on the base plate directly under the ram and over a hole to allow the extruded rod to pass through the plate. The positioning of the barrel is accomplished simply by pushing the barrel firmly against three pins set tangentially along the circumference of a circle having the same diameter as the barrel. The angular distance between each pin being approximately 50° .

The extrusion ram is placed on top of the extrusion barrel and off to the side enough so that it is clear of the inside diameter of the barrel. The press ram is then run down until it is only a fraction of an inch above the top of the extrusion ram.

The coextrusion can and the material to be extruded are heated, either separately or together depending upon temperature requirements, and are then quickly placed in the extrusion barrel.

Experimental Work

The work performed during this period was concerned mainly with testing the operation of the hot extrusion apparatus. The proper operation is somewhat complex and depends largely upon timing and teamwork of a group of three or four men. This is necessary to accomplish the extrusion as rapidly as possible before too much heat is lost to the cold extrusion barrel.

For this preliminary work, it was decided to use a material that had relatively well known flow properties and which would extrude at a lower temperature than barium titanate.

During this period three extrusion attempts were made. The ceramic material used was a proprietary, glass containing composition used in producing transfer molded parts. This material was chosen since the temperatures at which it can be transfer molded are known.

The mix was hand tamped into a coextrusion can of 1018 steel and placed in an electric furnace to heat. The die and barrel of the extruder were lubricated with a mix of graphite and stearic acid in CCl_4 . After soaking for about 10 minutes at the desired temperature, the coextrusion can was removed from the furnace and quickly placed in the extrusion barrel. The extrusion ram was placed in the barrel and the full extrusion pressure applied as rapidly as possible. The time between removal of the can from the furnace and application of full pressure was approximately 5-7 seconds. Neither the die nor the extrusion barrel were preheated. The temperatures to which the material and coextrusion can were heated were 1400, 1500 and 1700°F.

Discussion of Results

Extrusion did not occur on any of the three extrusion attempts. In fact there was very little difference in the appearance of the three slugs after the attempted extrusion. In each case, the coextrusion can did deform sufficiently to take the shape of the die and barrel and each had a slight "nose" where the can had been forced a short distance into the straight portion

of the die. The ceramic itself did not appear to have been heated sufficiently prior to the attempted extrusion since all pieces were porous although the porosity of the piece preheated to 1700°F was quite low. It appears that a ten minute soak at peak temperature is not sufficient for thoroughly heating the ceramic powder. This is probably due to its low thermal conductivity.

Conclusions

The preliminary hot extrusion attempts have shown, at least tentatively, that:

1. Using the present design of equipment, assembly of the necessary parts and application of full extrusion pressure can be obtained within 5 to 7 seconds after removal of the pieces from the furnace.
2. A soaking time of ten minutes is apparently not long enough to allow the ceramic extrusion blank to reach equilibrium.
3. The use of a coextrusion can having a softening temperature than 1018 steel is desirable for use in extruding the composition employed in the present study.

Future Work

A number of extrusion experiments will be performed using 1100-F aluminum. Trial runs will be made to determine the temperature and pressures needed for extrusion of solid slugs of

this aluminum. This will help in determining the parameters necessary for coextrusion of the aluminum with the ceramic material. According to the literature the aluminum should extrude between 750 and 900°F.² It is felt that the present extrusion apparatus will probably work most favorably if the coextrusion can is made of a metal which will extrude at a lower temperature than the ceramic since the coextrusion can is in direct contact with the cold barrel and die of the extruder during the extrusion period. If the ceramic is heated to a higher temperature than the coextrusion can it will act as a source of supply of heat to the can during the extrusion and, it is hoped, that this will enhance extrusion. If this method produces successful extrusions, a similar approach will be tried in the hot extrusion of barium titanate, choosing a coextrusion metal which has a higher extrusion temperature than aluminum. If it becomes apparent that the cooling of the coextrusion can by the room temperature extrusion barrel and die is greatly hampering successful extrusion, preheating of the barrel and die will be tried. In this case, care must be taken not to get the barrel and die hot enough to cause them to lose their temper.

2. Herbert R. Simonds, Archie J. Weith and William Schack, "Extrusion of Plastics, Rubber and Metals," Reinhold Publishing Corp., New York City, 1952.

Another method which may be used if the previous methods are not satisfactory will require a slight modification of the present assembly. The method consist essentially of having a liner made which can be preheated and placed inside the extrusion barrel just prior to the extrusion attempt. The coextrusion can will fit inside of this liner. The liner should be made of a material which will not flow at the extrusion temperature. It will serve as a buffer between the cold die and the coextrusion can thus keeping the temperature of the can from dropping so rapidly during the time required for extrusion.

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INORGANIC DIELECTRICS RESEARCH by J. H. Koenig, E. J. Smoke, C. J. Phillips, et al, SIGNAL CORPS REPORT NO. VI, November 1, 1961 to February 1, 1962. (Contract DA-36-039-sc-89141).
Unclassified report

Under Low Loss Microwave Ceramic Dielectrics three compositions in the $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system were hot-pressed and the electrical properties measured at several frequencies and temperatures. A study of the crystalline phases appearing in the compositions evaluated thus far revealed two lanthanum silicates, lanthanum aluminate and mullite. Attempts to form each lanthanum silicate compound by itself are being made in order to determine their

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