U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1703

Part of Journal of Research of the National Bureau of Standards, Volume 36, March 1946

STUDIES OF BINARY AND TERNARY COMBINATIONS OF MAGNESIA, CALCIA, BARIA, BERYLLIA, ALUMINA, THORIA AND ZIRCONIA IN RELATION TO THEIR USE AS PORCELAINS

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ABSTRACT

Specimens formed by pressing were heated and tested for absorption and shrinkage to determine the vitrification range. These pressed specimens represented the various oxides in simple binary and ternary combinations and also with minor additions of auxiliary oxides. Vitrified pieces were tested for strength in compression, thermal conduction and expansion, electrical resistance, dielectric properties, water solubility, and resistance to attack by PbO liquid and vapor. Several compositions of unusual and valuable properties were disclosed. Phase relations were approximated by fusion tests and petrographic examinations of nonquenched samples.

CONTENTS

I. INTRODUCTION

Conventional pottery bodies, which may be considered as including all types of ware from coarse earthen utensils to the most refined china or porcelain, are very complex and are composed of crystalline silicates in a matrix or bond of glass. Since time immemorial these bodies have been dependent upon this bond of glass for the mechanical strength and dense structure necessary to their usefulness. This glass is essentially an alkaline, or alkaline earth, silicate usually derived from some form of feldspar in the raw batch. Like all glasses, it does not have a sharply defined fusion point but will soften, and deform under stress, at temperatures much lower than the temperature at which it becomes entirely liquid, and also much lower than the temperatures at which the crystalline phases of the body liquefy. The glass in addition, is likely to have other characteristics, such as thermal expansion, that differ from those of the crystalline phases.

If the pottery is intended for tableware, or even for cooking purposes in the relatively mild temperatures of a wood fire or a baking oven, the presence of a glass bond is no detriment to its utility. The presence of glass is detrimental, however, if the ware is subjected to stress at greatly elevated temperatures, or to thermal shock. Furthermore, the possibility of reducing mechanical strength because of internal stresses caused by differences in thermal dilation, or even by differences in shrinkage during the initial heating in the kiln, applies not only to a glass-crystalline system but also to a polyphase all-crystalline system. Theoretically, therefore, the desideratum is a monophase crystalline body, preferably of fine structure so as to avoid coarse intercrystalline surfaces that may be planes of weakness.

What may have been the earliest departure from the feldspathic compositions was the attempt by Hecht [1] [1] to produce a more nearly glass-free porcelain. In 1907 Bell [2] introduced free alumina into porcelain mixtures but retained a considerable percentage of feldspar. A further improvement in composition was the so-called Marquardt porcelain, made at the Royal Porcelain Factory in Berlin. In his reference to this porcelain, Howat [3] gave, as its composition, 35.12 percent of SiO_2, 63.20 percent of Al_2O_3, and 1.65 percent of K_2O. It is obvious that the composition was intended to produce a single-phase crystalline body because, at the time of World War I, it was thought that alumina and silica combined in artificial mixtures to form the silicate found in nature as sillimanite ($Al_2O_3.SiO_2$) containing 37 percent of SiO_2 and 63 percent of Al_2O_3. Consequently, investigators had as their object the production of porcelains with as high a percentage of sillimanite as it was practicable to obtain under industrial conditions.

Some years later [4] it was shown that sillimanite does not form in artificial preparations and that the ideal monophase aluminum silicate body is composed of mullite ($3Al_2O_3.2SiO_2$). Mullite contains 28.2 percent of SiO_2, 71.8 percent of Al_2O_3, and fuses at 1,810° C. Many porcelains manufactured today for exacting service conditions are essentially mullite, but contain interstitial glass resulting from reactions with fluxes added to make possible the vitrification of the body at manufacturing costs commensurate with the market value of the ware. Although the mullite body is giving good service in spark plugs, thermocouple protection tubes, chemical ware, and other articles for special uses, investigators have not relented in their search for other simple oxide combinations that can be used at temperatures exceeding even the fusion point of mullite.

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[1] Numbers in brackets indicate the literature references at the end of this paper.

This search had been under way for some years as shown, for example, by English patents [5] covering the fabrication of articles from BeO, ThO_2, and ZrO_2. In Germany, interest in zirconia was very active as early as 1910 [6], and in this country the use of thoria crucibles for the refining of rhodium was described in 1929 [7]. The development of ceramic bodies of simple composition from pure oxides was not confined to the relatively rare oxides, and in 1929 German Patent No. 560,575 was granted for the making of articles from "aluminum oxide of high purity without special bonding agents." In 1924 the forming of shapes entirely from these nonplastic materials without the use of contaminating bonds was still beset with many difficulties according to Ruff [8] but, in 1935, Ryschkewitsch [9] stated that "the production of spark plug insulators of purest alumina, and single- or double-holed tubing of only a few tenths of a millimeter cross section of either beryllia or alumina, no longer presents a problem." The statement was too optimistic, but it did evidence an appreciable advance in the art. Many others have been active in this field during the past 15 years [10].

Under the impetus of the recent war, the generation and transmission of energy with greater and greater efficiency, and in ever-increasing quantities, is placing correspondingly greater demands upon engineering materials of all kinds, including ceramics. One illustration is the modern aviation engine, for which the spark plug of 20 years ago would be quite inadequate, and in which the practically single-phase alumina insulator is now used. Other developments, of which most are still on the restricted list of ordnance projects, either use ceramics that have been originated in recent years or have opened vistas of tremendous future possibilities for this type of material. In order to supply the fundamental information upon which the practical work of producing ceramics to meet these future possibilities can be based, there was undertaken a study of the characteristics of variously heated binary and ternary combinations of MgO, CaO, BaO, BeO, Al_2O_3, ThO_2, and ZrO_2, both as practically pure oxides and with minor additions of CaO, SrO, BaO, B_2O_3, SiO_2, TiO_2, or PbO. A preliminary report was published in 1941 [11], and the present paper reports results obtained since that time.

II. MATERIALS

In most cases the materials were the purest available commercially, but some oxides were especially prepared to further decrease contamination, as shown by the following descriptions. As prepared for use, the materials were in all cases at least sufficiently finely divided to pass the No. 325 U. S. Standard Sieve.

Alumina (Al_2O_3).—(1) Commercial grade usually used in making porcelain specimens and containing at least 99 percent of Al_2O_3 by analysis. Spectrograms showed medium strong lines for boron, weak lines for copper (probably abraded from the sieve), for sodium, and for silicon, and traces of several other elements.

(2) Laboratory prepared and usually used in bodies for fusion-point and softening-range determinations; obtained by dissolving aluminum of over 99.95-percent purity in nitric acid and igniting to the oxide. Spectrograms showed only very weak lines and traces of elements other than aluminum.

Barium oxide (BaO).—Introduced as reagent quality $BaCO_3$.

Beryllia (BeO).—(1) Commercial "SP grade," usually used in making the porcelain specimens, and nominally of 99.7-percent purity. Spectrograms showed only traces of copper, iron and magnesium, and very weak lines for silicon.

(2) Commercial "CP grade," usually used in specimens for fusion-point and softening-range determinations, nominally of over 99.9-percent purity.

Calcium oxide (CaO).—Introduced as reagent quality $CaCO_3$.

Magnesium oxide (MgO).—(1) Fused MgO (periclase) of approximately 97-percent purity, usually used in making porcelain specimens.

(2) Calcined $MgCO_3$ (calcining temperature given by producer as 2,000° F). Very fine grained, purity about 99 percent, and used in a relatively small number of specimens.

(3) Especially selected, water clear, crystals of periclase,[2] which were hand ground in agate or mullite mortars and usually used in bodies for fusion-point and softening-range tests. The purity is nominally over 99 percent.

Silica (SiO_2).—Pulverized natural quartz of 99.6-percent purity.

Strontia (SrO).—Introduced as reagent quality $SrCO_3$.

Titania (TiO_2).—Trade designation "pigment grade," purity about 99 percent, with Fe_2O_3 given by the producer as less than 0.2 percent.

Thoria (ThO_2).—Calcined thoria, nominally of over 99-percent purity. Spectrograms showed only very weak lines for calcium, copper, and silicon, and no other impurities were indicated.

Zirconia (ZrO_2).—A CP grade of calcined zirconia, and recalcined at 1,440° C. The spectrogram showed medium lines for columbium and titanium and only very weak lines or traces for calcium, copper, iron, magnesium, lead, and silicon.

In order to obtain the desired fineness of particle size, it was necessary to grind the SP BeO, the commercial grade Al_2O_3, and the ThO_2. The BeO described above had been ground wet for 2 hours in porcelain-lined mills with flint pebbles. The Al_2O_3 and the ThO_2 had been ground for 48 hr. in a steel mill with steel rods, and then purified by treatment with diluted HCl until the wash water gave a negative test for iron.[3]

III. METHODS

Specimens were prepared during the first stages of the work by hand-mixing the ingredients in slip form, drying, pulverizing in an agate or in a mullite mortar, remixing with a 5-percent solution of soluble starch, and pressing in hardened steel moulds. About 14 g of the starch solution was used for 100 g of dry batch, and the forming pressure was 9,300 lb/in^2. Later, the method was improved by machine-blunging the slip with a chemical-laboratory-type stirrer, and by vibrating the dampened mixture in the steel moulds before pressing. The pressed specimens were matured in an electric furnace, heated with eight ThO_2-Y_2O_3 resistors, described in Bureau Research Paper RP1662 [12]. The heating and cooling rates were maintained very close to 3°C per min, and the holding time at the maximum temperature usually was 1 hr. A typical setup with three specimens

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[2] Furnished by the Vitrefrax Corporation and by the Norton Co.

[3] Comparative tests were made also on specimens of mixtures containing ThO_2 that had been fused in an electric arc, ground in the steel mill, and acid-treated, but the results reported are for bodies made with the calcined thoria only.

for the crushing test is shown in fig. 1, *A*. All temperature measurements in the maturing treatment, and also in the softening-range and melting-point tests, were made with a Leeds & Northrup optical pyrometer calibrated at the Bureau.

For the softening-range and fusion tests, small four-sided pyramids about $^{3}/_{16}$ in. at the base and grooved on each side, as shown in figure 1, *B*, were ground from pressed, unfired pieces and were tested in the furnace described in Bureau Research Paper RP1443 [11]. The furnace arrangement for softening-range and fusion tests is shown in figure 1, *C*. The specimen rests upon a disk of rhodium, or of 20 percent rhodium–80 percent platinum, depending upon the maximum temperature to be reached, and the metal disk in turn is supported on a pedestal of ZrO_2, ThO_2, or BeO. By careful placement of the disk so that its flat (or slightly concave) upper surface is perpendicular to the line of vision, an effect is obtained in which the metal surface reflects less light to the pyrometer than the specimen does. As a result, the metal appears slightly colder than the specimen and makes it visible in outline. For a typical specimen, this outline will appear as shown at the top in figure 1, *B*, except that the diagonals representing the edges from base to apex would not be visible. The temperature rise as the fusing temperature was approached, and during fusion, was held as close as possible to a rate of from 1° C to 2° C per min.

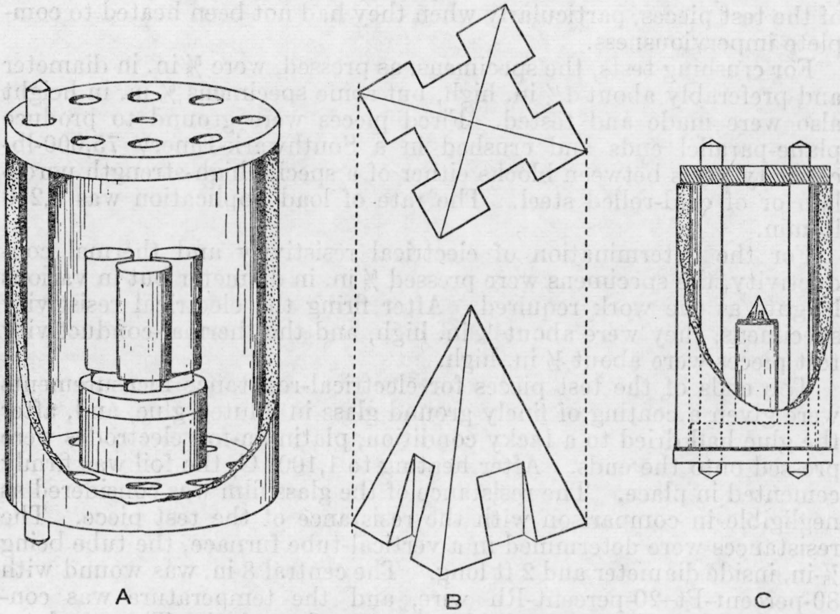

FIGURE 1.—*Furnace arrangements for heating specimens.*

A, Setup for heating three specimens to vitrification. Specimens measure about 0.55 in. in diameter by 1.1 in. long, and rest on platinum-rhodium disks. They are shown in the heating chamber of an eight-resistor furnace, described in J. Research NBS **35** 87 (1945) RP1662.

B, Shape of specimen for fusion tests. These were ground from pressed blanks and measure about $^{3}/_{16}$ in. square at the base.

C, Specimen for fusion test, shown in the three-resistor furnace described in J. Research NBS **27** 555 (1941) RP1443. The specimen rests on a rhodium plate supported by a ThO_2, ZrO_2, or BeO pedestal.

Shrinkage values were based on micrometer measurements of the diameter of specimens when dry, and after having been fired. Absorption values were obtained by boiling the fired specimens in carbon tetrachloride for 5 hr, permitting them to cool in the liquid until the next day, and determining the increase in weight. The weight increase was divided by the density of the CCl_4 in order to make the values comparable with data obtained conventionally by boiling the specimens in water. CCl_4 was used as the saturating medium because preliminary tests with water had shown appreciable solution of some of the test pieces, particularly when they had not been heated to complete imperviousness.

For crushing tests, the specimens, as pressed, were ⅝ in. in diameter and preferably about 1¼ in. high, but some specimens ⅝ in. in height also were made and tested. Fired pieces were ground to produce plane-parallel ends and crushed in a Southwark-Emery 75,000-lb-capacity press between blocks either of a special high-strength porcelain or of cold-rolled steel. The rate of load application was 6,250 lb/min.

For the determination of electrical resistivity and thermal conductivity, the specimens were pressed ⅝ in. in diameter but in various heights as the work required. After firing the electrical resistivity specimens, they were about ⅛ in. high, and the thermal-conductivity test pieces were about ½ in. high.

The ends of the test pieces for electrical-resistance measurements were given a coating of finely ground glass in diluted glue, and, after the glue had dried to a tacky condition, platinum-foil electrodes were pressed onto the ends. After heating to 1,100° C, the foil was firmly cemented in place. The resistance of the glass film was considered as negligible in comparison with the resistance of the test piece. The resistances were determined in a vertical-tube furnace, the tube being ⅞-in. inside diameter and 2 ft long. The central 8 in. was wound with 80-percent-Pt–20-percent-Rh wire, and the temperature was controlled with a Wheatstone bridge-type regulator [13]. This regulator maintained an average temperature to ± 0.1 deg C, and the variation over the test piece, during the 10 min that a specimen was held at a given temperature before a resistance measurement was made, did not exceed ± 1.5 deg C.

In the furnace, the test specimen was held at the center of the hottest section between platinum electrodes affixed to the ends of mullite tubes, through which the thermocouple and connecting wires were placed. These tubes were concentrically located in the furnace tube by means of alumina guide disks. Resistances were measured on a Weston ohmmeter, model 764, and a 60-cycle current of a few microamperes was put through the test piece, thus avoiding polarization and also any appreciable heating effects from the measuring current. The lead wires from the instrument to the furnace were kept well separated to minimize capacitance-conductance effects. This method was devised by E. N. Bunting.

The resistance was assumed to be largely volume resistance, for which the specific value may be expressed as $\rho = RA/L$, where R is the measured resistance in ohms, A is the area of the end of the specimen in square centimeters, and L is the average thickness of the specimen in centimeters. Resistance measurements were usually made at 25 deg C intervals. By plotting log ρ against temperature, an approximately straight line was obtained, represented by the equation $\rho = c - bt$, where c and b are constants, and t is in degrees centigrade. The T_e value, which is the temperature at which ρ equals 1 megohm, could then be obtained by interpolation from this line.

The thermal-conductivity values are purely relative, and are expressed as 100 times the reciprocal of the temperature drop in degrees centigrade across a one-half-inch height of specimen approximately one-half inch in diameter when resting on a hot plate with a surface temperature of 250° C. This hot plate was an aluminum disk, 8 in. in diameter by 0.5 in. thick, which rested on an insulated heating coil, 4 in. in diameter, to which current was supplied from a constant-voltage transformer. This coil, in turn, was supported on a pedestal of insulating refractory, and the entire arrangement was located centrally in a cubical cabinet having a volume of 8 ft^3.

The matured specimen was prepared by grinding the ends plane-parallel and 0.5 in. apart. A diametrical groove was then ground in each end to a depth sufficient to take a copper-constantan thermocouple of 0.01-in.-diameter wire. A couple was cemented into each groove, with the hot junction at the center of the groove, and a "cap" was fastened to the top end of the specimen with a minimum of cementing material. This cap was made by grinding another one-half-in.-diameter piece of the same composition as the specimen so that the ends were plane-parallel and about ¼ in. apart. Several such assemblies of specimen and cap could be placed simultaneously upon the hot plate and the ends of the thermocouples carried to junctions outside the cabinet. The current was regulated to give a temperature of 250° C when read with the thermocouple located in the end of a specimen resting on the hot plate. When the entire setup had reached equilibrium, the temperature drop between the "hot-plate couple", and the couple between the specimen and the cap was recorded for each specimen assembly.

Determinations of relative resistance to the attack of PbO[4] were made in two ways, using specimens which had been pressed ⅝ in. in diameter and ½ to ¾ in. high. In one, the PbO was placed in a 25-ml platinum crucible and covered with a regular platinum crucible cover through which several large holes had been drilled. The weighed specimen, supported by a small tripod of BeO, was placed on the lid and covered with an inverted 25-ml platinum crucible. The entire assembly was placed within an electric furnace, using 80-percent Pt–20-percent Rh as the resistance element, and heated for 4 hr, usually at 1,100° C. After this treatment, the specimen, together with a comparable untreated piece or "blank" of the same composition, was immersed in a 1-to-1 solution of HNO_3 on a hot plate for about 16 hr, washed, redried at 500° C, and weighed. In the other method, the lid between the two crucibles was omitted and the specimen placed directly in the molten PbO. Because the specimens floated on the molten PbO and were only partly immersed, numerical values are not comparable, and resistance to solution was judged by inspection.

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[4] These determinations were designed to measure the relative resistance to attack of a porcelain in vapors containing lead oxide. Such vapors are found in the cylinders of internal-combustion engines using a fuel with an admixture of tetraethel lead.

For the thermal-expansion tests, using the interferometer method [14], disks about 3/16 in. high and 1 in. in diameter were first matured and then ground to the shape of a V with raised portions, or feet, on both sides at the apex and at the end of each leg.

Specimens for the determination of dielectric constant and power factor were pressed 1⅝ in. in diameter and about 3/16 in. in height. The tests were made by C. M. Sparks and Arnold H. Scott in the Inductance and Capacitance Section of the Bureau, using the bridge and the method described in Bureau Research Paper RP1457 [14a].

The fact that many of the temperatures involved in the phase studies were above the melting point of platinum would greatly increase the mechanical difficulties of efficiently quenching the specimens. For the phase studies reported here, the preparations examined were obtained mostly from fusion determinations. Their firing time was comparatively short; many were not fused completely to liquid, and none was quenched. Therefore, it is apparent that equilibrium was obtained only rarely, and the equilibrium conditions at elevated temperatures were not established. With this in mind, the proposed phase relations were based primarily on fusion behavior. The fusion behavior of the compositions, combined with petrographic and X-ray examinations, is, however, believed to be strongly indicative of the true equilibrium conditions.

IV. RESULTS

1. THE SYSTEM BeO-Al_2O_3

A paper by Wartenburg and Reusch [15] on the system BeO-Al_2O_3 reports a simple eutectic at 80 wt percent of Al_2O_3 and 1,890° C, with no indication of a compound. Their determinations involved rapid fusion to a bead in an oxypetroleum flame and also rapid cooling. In the present investigation the compound $BeO.Al_2O_3$, corresponding to the mineral chrysoberyl, was obtained readily either by sintering or by fusing the intimately mixed oxides. The results indicate also a eutectic at about 1,880° C and 14 wt percent of BeO and at about 1,865° C and 27 wt percent of BeO, as shown by the following data.

A mixture in equimolar ratio of SP BeO and the commercial Al_2O_3 (19.7 and 80.3 wt percent, respectively) fused at 1,880° C and crystallized in laths, some of which were as large as 1 by 3 mm. These laths were chrysoberyl and had the following optical properties: biaxial +; optic angle about 45°; indices of refraction—alpha 1.747, beta 1.748, gamma 1.756. A similar mixture, using CP beryllia and the laboratory-prepared alumina, fused at 1,890° C and crystallized as long, clear prisms of chrysoberyl with properties as given for the crystals in the less pure mixture. With the same pure oxides, the mole composition $BeO:4Al_2O_3$ (5.78 wt percent of BeO) fused at 1,920° to 1,925° C; $BeO:2Al_2O_3$ (10.9 wt percent of BeO) fused between 1,885° and 1,900° C; $2BeO:3Al_2O_3$ (14.06 wt percent of BeO) fused at 1,880° to 1,885° C; $1.5BeO:Al_2O_3$ (26.91 wt percent of BeO) fused sharply at 1,865° C; $2BeO:Al_2O_3$ (32.9 wt percent of BeO) began to fuse at 1,875° C, but fusion was far from complete at 1,880° C; and $4BeO:Al_2O_3$ (49.5 wt percent of BeO) showed no fusion at 1,915° C.

The fusion behavior of the compositions between the chrysoberyl-beryllia eutectic and beryllia indicates solid solution. X-ray powder

TABLE 1.—*Values for physical and dielectric properties of binary compositions and component oxides*

Specimen from test No.	Composition						Matured at—	Number of specimens	Physical properties				Number of specimens	Absorption	Dielectric properties at 100 kc/s[c]	
	Mole			Weight					Absorption	Linear shrinkage	Bulk density	Compressive strength[b]			Constant	Loss angle
	MgO	BeO	Al_2O_3	Calcined MgO	SP BeO	Al_2O_3[a]										
				%	%	%	°C		%	%		lb/in.²		%	K	tanδ
106-L	0	0	1	0	0	100	1,875	2	0.18	11	3.69	71,000	2	0.11	9.1	0.0020
107-L	0	0	1	0	0	100	1,905	3	.18	11	3.73	62,000	-----	-----	-----	-----
110-L	0	0	1	0	0	[d]100	1,835	3	.18	11	3.73	156,000	-----	-----	-----	-----
99-L	0	0	1	0	0	[e]100	1,930	-----	-----	-----	-----	-----	2	.14	8.7	.0003
127-L	0	1	1	0	19.7	80.3	1,840	3	.01	9	3.23	119,000	-----	-----	-----	-----
155-L	0	1	1	0	19.7	[e]80.3	1,840	3	.01	[f]17	3.26	109,000	-----	-----	-----	-----
89-L	0	1	1	0	19.7	80.3	1,860	3	.04	9	3.27	119,000	-----	-----	-----	-----
121-L	0	1	1	0	19.7	80.3	1,865	-----	-----	-----	-----	-----	3	.00	[g]7.7	[g].0001
101-L	0	1	0	0	100.0	0	1,925	3	.03	18	2.79	128,000	2	.14	6.3	.0024
96-L	-----	-----	-----	1	99.0	0	1,850	3	.01	18	2.85	117,000	2	.01	6.5	.0007
128-L	1	10	0	13.8	86.2	0	1,830	1	.01	21	2.91	157,000	-----	-----	-----	-----
153-L	1	10	0	13.8	86.2	0	1,600	3	.02	22	2.86	94,000	-----	-----	-----	-----
117-L	1	0	1	28.3	0	71.7	1,950	3	.26	6	3.15	99,000	3	.02	7.2	.0037

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[a] Commercial Al_2O_3, except as noted.

[b] The compression tests were made with the nominal 0.5-in.-diameter by 1-in.-long specimens between contact blocks of special high-temperature porcelain (see table 2).

[c] The dielectric values were determined by C. M. Sparks and A. H. Scott.

[d] Decanted "fines" from commercial Al_2O_3.

[e] Laboratory-prepared Al_2O_3 of 99.95-percent purity.

[f] This comparatively high shrinkage is accounted for by the fact that the Al_2O_3 used in the mixture was the calcined laboratory-prepared material of 99.95-percent purity.

[g] Fired-on silver electrodes.

patterns do not support this, but they do support the assumption that no other compound of BeO and Al_2O_3 is formed. Petrographic and X-ray examinations also revealed that only one phase ($BeAl_2O_4$) was present in samples of $2BeO{:}3Al_2O_3$, $BeO{:}2Al_2O_3$, and $BeO{:}3Al_2O_3$. The absence of alumina in these specimens indicates that solid solution had occurred. In the composition $BeO{:}4Al_2O_3$, inclusions of alumina were present as rounded grains of corundum. The crystallographic evidence is, therefore, that chrysoberyl can take at least 2 moles, but not 3 moles, of alumina into solid solution.

Three tests on two vitreous pieces of $BeAl_2O_4$ produced T_e values ranging from 1,270° to 1,285° C, and six observations of thermal conductivity on one of these pieces gave an average value of 3.4. Specimens for the determination of absorption, shrinkage, strength in compression, and dielectric properties were heated at 1,840° to 1,865° C (table 1). Chrysoberyl specimens of uniformly fine crystal texture were not obtained. Even 1,840° C, the minimum temperature for complete vitrification,[5] produced also an undesirably coarse crystal texture. For example, one of several rods of $BeAl_2O_4$, heated at 1,840° C for 1 hr, contained crystals ranging in size from 20 to 3,000 microns (fig. 2). This particular specimen had an absorption of less than 0.01 percent and failed in the crushing test at 114,000 lb/in^2. Average values for nine similar specimens are given in table 1.

The crushing tests were made with the specimen between porcelain blocks. Experiments made later in the investigation, and recorded in table 2, proved that the maximum compressive strength was not developed with the porcelain blocks and that more consistent, and significantly higher, values can be obtained with cold-rolled-steel blocks. The two porcelains referred to in table 2 are commercial compositions, and the test pieces were made under very carefully controlled industrial conditions. Preliminary tests demonstrated also that steel blocks ½-in. in thickness were not suitable (fig. 3), and the reported values were obtained with blocks three-quarter-inch thick. In addition to showing the advantage of using steel blocks, the values given in table 2 show that higher values were obtained for specimens with a length to diameter ratio of about 2:1, as compared to those with a ratio of about 1:1, and for glazed as compared to unglazed specimens.

The following values were obtained for the average coefficients of linear thermal expansion of chrysoberyl (multiply the values by 10^{-6}): Room temperature to 100° C, 5.6; 100° to 200° C, 7.1; 200° to 300° C, 7.8; 300° to 400° C, 8.7; 400° to 500° C, 9.6; 500° to 600° C, 9.8; 600° to 700° C, 9.7; 700° to 800° C, 9.8; 800° to 900° C, 8.8; and 900° to 1,000° C, 9.2. The percentage expansion from room temperature to 1,000° C was 0.788.

A limited number of tests were made on specimens composed entirely of BeO or of Al_2O_3 (table 1). Very small percentages of impurities have a pronounced effect on the vitrification behavior of beryllia. The SP grade could be vitrified at 1,800° C, but the CP grade showed an absorption of 20 percent at 1,800° and 6.1 percent at 1,900° C. Some photomicrographs of typical crystal growths for both types of Al_2O_3 are shown in figures 4 and 5, and representative values for strength in compression, and for dielectric constant and loss angle, are given in table 1. The T_e value for three vitreous specimens of

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[5] In this investigation, a completely vitrified structure is defined arbitrarily as one having an absorption of less than 0.1 percent.

FIGURE 2.—*Photomicrograph, taken with crossed polarized light, showing crystal development in a specimen of chrysoberyl* ($BeAl_2O_4$) *heated at 1,840° C.*

The distance between the arrow points at the left represents a length of 1 mm.

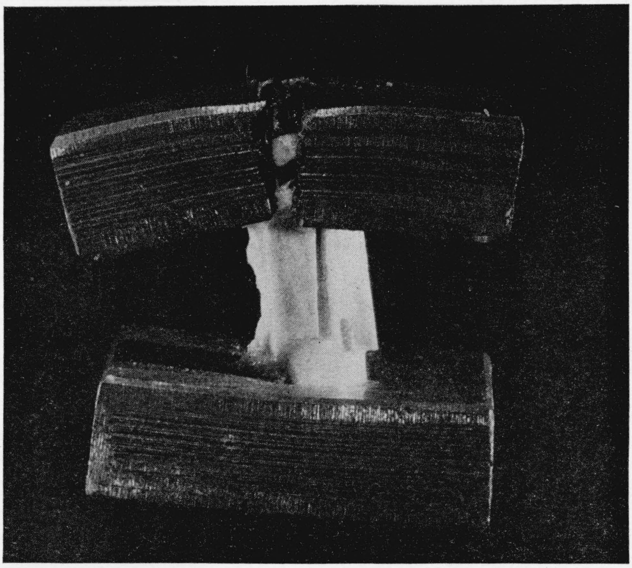

FIGURE 3.—*Penetration and rupture of a ½ in. thick cold-rolled steel block by a ½-in. diameter specimen of a commercial porcelain during test in compression. The porcelain failed at 332,000 lb/in*^{2}.

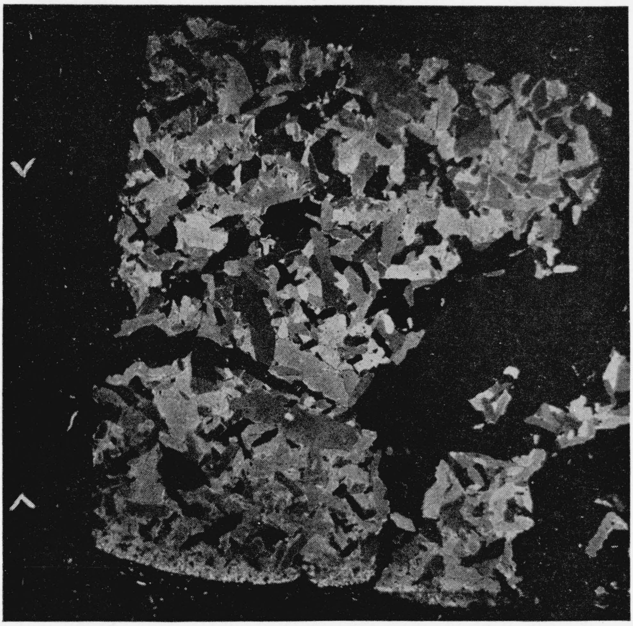

FIGURE 4.—*Photomicrograph, taken with crossed polarized light, showing crystal development in a specimen of commercial alumina heated at 1,905°C.*

The distance between the arrow points at the left represents a length of 1 cm.

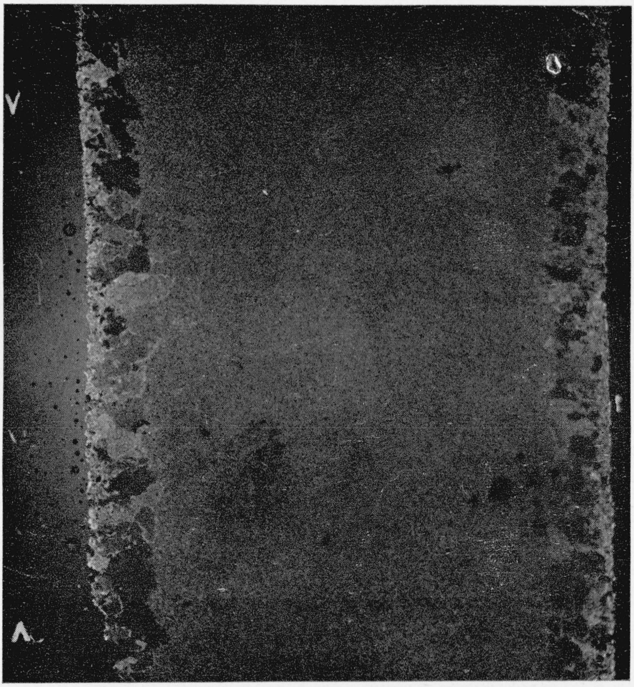

FIGURE 5.—*Photomicrograph, taken with crossed polarized light, showing crystal development in a specimen of laboratory-prepared alumina (99.95 percent* Al_2O_3*) heated at 1,890°.*

This is a longitudinal section of a rod. At the original outer surface, and to a depth of about 0.7 mm, the crystals average 30 microns in size. The next concentric layer, about 1.5 mm wide, contains crystals averaging 400 microns in size. The center portion is very fine grained, the crystals averaging about 5 microns in size.

The distance between the arrow points at the left represents a length of 1 cm.

commercial alumina ranged from 1,076° to 1,167° C. For two specimens of the laboratory-prepared alumina the values were 1,102° and 1,186° C, and for an artificial single crystal,[6] the value was 1,214° C parallel to, and 1,231° C, perpendicular to, the *c* axis. For one specimen of BeO (table 3) the value was 1,177° C, for another it was 1,230° C. Nine observations of relative thermal conductivity on two alumina specimens gave the average value 3.6, and for two beryllia specimens (table 3) the value was 12.5.

TABLE 2.—*Effect of contact blocks, glazing, and length-diameter ratio of specimens on resistance to crushing*

Nominal length	Average length-diameter ratio	Number of specimens	Glazed	Contact blocks	Compressive strength
			Porcelain No. 3		
In.					*lb./in.*^{2}
1	2.13	5	Yes	Cold-rolled steel	316,000±12,000
½	1.15	11	do	do	271,000±8,000
1	2.15	5	do	Porcelain	231,000±24,000
1	2.18	5	No	do	205,000±26,000
1	2.13	5	Yes	Cold-rolled steel	316,000±12,000
1	2.20	4	No	do	298,000±24,000
1	2.15	5	Yes	Porcelain	231,000±24,000
1	2.13	5	do	Cold-rolled steel	316,000±12,000
1	2.18	5	No	Porcelain	205,000±26,000
1	2.20	4	do	Cold-rolled steel	298,000±24,000
			Porcelain No. 4		
1	2.06	4	Yes	Porcelain	215,000±25,000
½	1.01	6	do	do	170,000±12,000
1	2.01	4	do	Cold-rolled steel	303,000± 3,000
½	1.03	8	do	do	262,000±10,000
1	2.01	4	do	do	303,000± 3,000
1	2.10	12	No	do	262,000±10,000
1	2.06	4	Yes	Porcelain	215,000±25,000
1	2.01	4	do	Cold-rolled steel	303,000± 3,000
½	1.01	6	do	Porcelain	170,000±12,000
½	1.03	8	do	Cold-rolled steel	262,000±10,000

2. THE SYSTEM MgO-BeO

In 1937, Wartenburg and coworkers [16] reported a simple eutectic at 1,860° C and 50 wt percent of BeO. This is in good agreement with the results of the present investigation, in which the mixture containing 48.2 wt percent of BeO (MgO:1.5BeO mole ratio) fused sharply at 1,855° C. In comparison, mixtures with 38.3 wt percent (MgO:BeO mole ratio), 55.4 wt percent (MgO:2BeO mole ratio), and 65.1 wt percent of BeO (MgO:3BeO mole ratio) were not completely fused after holding at 1,875° C. The following petrographic report contains no evidence of solid solution or of compound formation in this system, and is in accord with the indication of the fusion tests that the mole composition MgO:1.5BeO is at, or very near, the eutectic:

MgO:BeO (*heated at 1,860° C*).—The texture was characteristically in a radial, or fan shaped, arrangements of crystals resulting from the co-crystallization of thin plates of MgO and BeO. The core of these

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[6] Furnished by the Linde Air Products Co.

fan shapes is composed of MgO. This composition is definitely on the MgO side of the eutectic, as shown by the presence of free magnesia grains.

MgO:1.5BeO (*heated at 1,855° C*).—The core of the fan-shaped formations is composed of BeO and of MgO crystals as polygonal sintered grains. The outer portions consist mainly of BeO and MgO in intergrowth texture. This composition appears to be at, or near, the eutectic.

MgO:2BeO (*heated at 1,875°*).—Crystals at the edge of the specimen show an unusual texture made up of irregular plates of BeO and MgO in alternate positions. The core of the fan-shaped crystal growths is predominantly BeO.

MgO:3BeO (*heated at 1,875°*).—The crystals are rounded in appearance and have a botryoidal structure. They are composed of BeO and MgO in intergrowth texture. Judging from the relative amounts of this texture, this specimen is further from the eutectic than is MgO:2BeO.

Compositions containing not more than about 21.2 wt percent of MgO (mole ratio MgO:6BeO) could be vitrified. The temperature range over which vitrification was attained decreased with increase in MgO content, and all the vitrified bodies had a relatively coarse crystal texture, the tendency being for the coarseness to increase with increase in percentage of MgO and with increase in the temperature of heating. Composition MgO:10BeO was typical and consisted of MgO in a fine mosaic, with BeO in rounded and irregular grains averaging about 15 microns in size, when heated at 1,560° C. When heated at 1,850° C, the MgO was present in small grains with cubic cleavage, and the BeO crystals had grown as large as 70 microns in maximum dimension. Four specimens were tested for strength in compression (see tests 128–L and 153–L, table 1), and values for electrical resistance and thermal conductivity are given in table 3.

TABLE 3.—*Absorption, linear shrinkage, electrical resistivity, and thermal conductivity values for* BeO, *for* MgO, *and for mixtures of these oxides*

Specimen from test No.	Composition				Matured at—	Absorption	Shrinkage	Electrical resistivity [a] (T_e value)	Thermal conductivity [b]
	Mole		Weight						
	MgO	BeO	MgO	BeO					
			%	%	° C	%	%	° C	
81–L	---	---	---	100	1,880	0.09	---	1,177	12.5
98–L	---	---	---	100	1,925	.03	19.0	1,230	12.5
39–L	---	---	1	99	1,875	.18	19.0	1,210	---
171	---	---	1	99	1,930	.01	20.0	1,191	12.5
33–L	---	---	2	98	1,875	.07	23.0	1,029	---
189	---	---	5	95	1,835	.03	17.6	1,200	12.5
140	1	15	9.7	90.3	1,855	[c]1.43	20.0	1,190	---
236	1	15	9.7	90.3	1,830	0.00	20.0	1,206	---
236	1	10	13.9	86.1	1,830	.01	20.6	1,169	12.5
234	1	4	28.7	71.3	1,835	.23	23.1	1,186	12.5
211	1	3	34.9	65.1	1,835	.37	16.8	1,150	7.1
214	1	2	44.6	55.4	1,835	.43	16.3	1,201	6.2
(d)	---	---	100	---	---	---	---	1,232	2.5

[a] The T_e value for electrical resistivity is the temperature at which, by calculation based on test values, a 1-cm cube of the material has a resistance of 1 megohm. The values were obtained by E. N. Bunting.

[b] These values are the reciprocal, multiplied by 100, of the temperature drop through a 0.5-in. height of specimen approximately ½ in. in diameter. The values were determined by E. N. Bunting.

[c] This value was obtained by boiling the specimen in water, causing partial hydrolysis.

[d] Specimen cut from a single crystal of periclase.

3. THE SYSTEM $MgO-Al_2O_3$

The system has been explored by Rankin and Merwin [17], and no work was done on it in this investigation beyond a limited number of tests on the compound $MgAl_2O_4$ (spinel). For some results, see test 117–L, table 1. In addition, a specimen heated at 1,900° C, and having an absorption of 0.10 percent, gave a thermal-conductivity value of 1.9, and for a section of this specimen, the T_e value was 1,170° C. It was noted also that when equimolar mixtures of MgO and Al_2O_3 were heated for 15 min at 1,700° C and at 1,800° C, the conversion to spinel was over 95 percent complete. Heating the mixture for the same length of time at 1,650° C caused 80- to 90-percent conversion. The following average coefficients of linear thermal expansion were obtained for a spinel sample that had been fired at 1,800° C (multiply values by 10^{-6}): room temperature to 100° C, 6.0; 100° to 200° C, 7.5; 200° to 300° C, 8.1; 300° to 400° C, 8.7; 400° to 500° C, 9.0; 500° to 600° C, 9.0; 600° to 700° C, 8.9; 700° to 800° C, 8.6; 800° to 900° C, 7.4; 900° to 1,000° C, 7.1. The specimen had reacted with the fused-silica interferometer plates, which may explain the decreasing coefficients for the temperature intervals above 600° C.

4. THE SYSTEM $MgO-BeO-Al_2O_3$

The only information found in the literature on this system is contained in patents [18]. The phase relations indicated by the fusion behavior of the 41 compositions examined in the present study are shown in figure 6. According to these indications, the greater por-

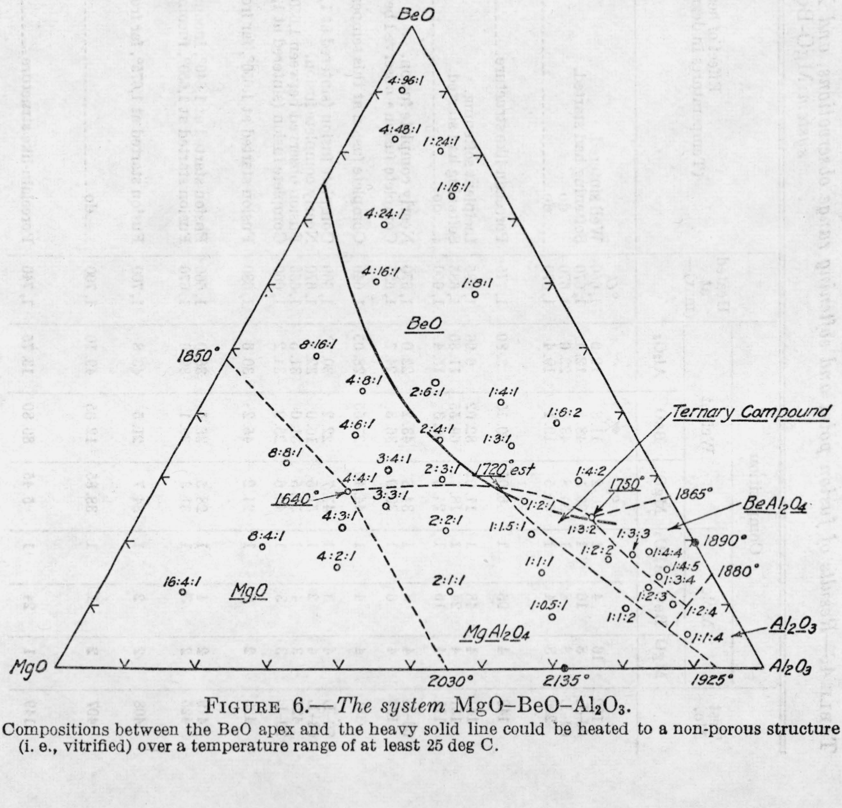

FIGURE 6.—*The system* $MgO-BeO-Al_2O_3$.

Compositions between the BeO apex and the heavy solid line could be heated to a non-porous structure (i. e., vitrified) over a temperature range of at least 25 deg C.

TABLE 4.—*Results of fusion point and softening range observations, and X-ray and microscopical examinations of the tested specimens in the system* MgO-BeO-Al_2O_3

Test No.	Composition						Heated at (max)—	Effect of heating (Temperatures in degrees centigrade)	Results of X-ray and microscopical examinations (Specimens examined were not quenched and the phases observed may not be those in equilibrium at the maximum temperature of heating or at the liquids)
	Mole			Weight					
	MgO	BeO	Al_2O_3	MgO	BeO	Al_2O_3			
				%	%	%	°C		
122	16	4	1	76.2	11.8	12.0	1,650	Well sintered.	
66–L	8	16	1	39.1	48.5	12.4	1,670	Softening had started.	
64–L	8	8	1	34.8	43.2	22.0	1,670	do	
226	8	4	1	61.5	19.1	19.4	1,670	do	Crystalline phases: periclase, bromellite and spinel. Mosaic texture. Average grain size 20 to 25 microns.
148	4	96	1	6.05	90.15	3.80	1,775	Porcelain-like structure	Bromellite, with rare grains of periclase and spinel. Grain size of bromellite 25 to 85 microns.
151	4	48	1	11.02	82.02	6.96	1,685	Incipient softening.	
151	4	24	1	18.65	69.55	11.80	1,685	Softening had started.	
111	4	16	1	24.3	60.3	15.4	1,650	do	X-ray pattern contains only lines for periclase, bromellite, and spinel.
63–L	4	8	1	34.8	43.2	22.0	1,670	Nearly complete fusion.	
194	4	6	1	39.0	36.3	24.7	1,655	Complete fusion[a] observed between 1,650° and 1,655°.	
351	4	4	1	44.40	27.55	28.05	1,640	Complete fusion at this temperature	X-ray pattern of specimen heated at 1,710° C gave only lines for periclase, bromellite, and spinel.
70–L	4	3	1	47.7	22.2	30.1	1,660	Complete fusion (sintered at 1,650°).	
63–L	4	2	1	51.5	16.0	32.5	1,670	Nearly complete fusion.	
426	3	4	1	37.5	31.0	31.5	1,655	Fusion observed between 1,650° and 1,655°.	
70–L	3	3	1	40.6	25.2	34.2	1,660	Complete fusion (sintered at 1,650°).	
423	2	6	1	24.2	45.2	30.6	1,680	Fusion started at 1,650°, far from complete at 1,680°	A specimen heated at 1,750° contained bromellite, and BeO with spinel in graphic intergrowths, indicating BeO as the primary phase.
419	2	4	1	28.5	35.5	36.0	1,660	Fusion started at 1,640°, incomplete at 1,660°	Do.
425	2	3	1	31.3	29.1	39.6	1,670	Fusion started at 1,650°, incomplete at 1,670°	A specimen heated at 1,660° C showed a "grating" texture interstitial to BeO crystals, indicating proximity to a field boundary.
408	2	2	1	34.7	21.5	43.8	1,700	Fusion started at 1,675°, far from complete at 1,700°	Crystals of BeO, spinel, and MgO in complete graphic form, indicating proximity to a field boundary. The specimen examined had been fused at 1,750° C.
407	2	1	1	38.85	12.05	49.10	1,700	do	Well-developed crystals of BeO and spinel in graphic intergrowth texture. Occasional irregular grains of MgO. Textural appearance indicates spinel as the primary phase.
149	1	24	1	5.45	80.80	13.75	1,740	Porcelain-like structure	Bromellite is the only crystal phase identified. Average range in grain size is 20 to 40 microns.

57-L	1	16	1	7.42	73.80	18.78	1,805	Softening had started.	
55-L	1	8	1	11.80	58.45	29.75	1,775	Complete fusion (started at 1,755°)	Bromellite, both in blocky grains and as intergrowths with spinel.
199	1	4	1	16.6	41.3	42.1	1,755	Complete fusion observed between 1,750° and 1,755°.	
197	1	3	1	18.55	34.55	46.90	1,750	Complete fusion observed between 1,745° and 1,750°	Well-developed crystals of bromellite and spinel in graphic texture.
198	1	2	1	21.0	26.0	53.0	1,760	Complete fusion between 1,755° and 1,760°	BeO in parallel orientation with spinel, possibly an unmixing texture. X-ray shows only lines for bromellite and spinel. For a specimen heated at 1,740°, both X-ray and petrographic examination showed the presence, in small percentage, of the "ternary" phase.[b]
422	1	1.5	1	22.45	20.90	56.65	1,745	Complete fusion observed between 1,740° and 1,745°	Crystals of bromellite and spinel in graphic texture.
55-L	1	1	1	24.10	14.96	60.94	1,775	Fusion nearly complete (started at 1,730°)	Do.
49-L	1	0.5	1	26.03	8.08	65.89	1,860	Softening had started	Spinel containing some bromellite in lath formation.
112-L	1	6	2	10.22	38.05	51.73	1,765	Well sintered	Spinel, BeO, and a third phase which could not be identified, but may be the "ternary" compound.
109-L	1	4	2	11.7	29.1	59.2	1,760	Fusion nearly complete	Principal phase may be ternary compound. Spinel and BeO also present.
421	1	3	2	12.65	23.50	63.85	1,750	Complete fusion between 1,748° and 1,750°	Principal phase may be ternary compound. Chrysoberyl ($BeAl_2O_4$) and BeO also present.
355	1	2	2	13.7	17.0	69.3	1,790	Complete fusion between 1,765° and 1,770°	About 60 percent is the possible ternary phase. Remainder, BeO, with rare grains of spinel. When heated at 1,850°, or fused in an oxyflame, product was over 98 percent large crystals of the "ternary" phase.
352	1	1	2	14.95	9.30	75.75	1,880	Fusion started at 1,830° and not complete at 1,880°	Apparently all one phase.[b]
119-L	1	3	3	9.6	17.8	72.6	1,750	Complete fusion observed between 1,755° and 1,760°	Crystals mostly the "ternary" compound, BeO intergrown with the "ternary" compound, and small amounts of chrysoberyl and spinel.
118-L	1	2	3	10.15	12.65	77.20	1,780	Complete fusion observed between 1,765° and 1,775°	Principal phase is spinel with the "ternary" phase second in quantity, and BeO rare.
47-L	1	4	4	7.35	18.25	74.40	1,800	Complete fusion at this temperature	Principal phase is chrysoberyl, with spinel and the "ternary" phase in small amounts.
240	1	3	4	7.70	14.35	77.95	1,810	Fused sharply at this temperature	Chrysoberyl 85 percent, spinel 10 percent, and rare grains of the "ternary" phase.
118-L	1	2	4	8.15	10.12	81.73	1,770	Softening had started	Corundum 15 percent, spinel 10 percent, remainder very fine-grained birefringent crystals.
50-L	1	1	4	8.5	5.3	86.2	1,855	do	Spinel, corundum, and chrysoberyl in about equal quantities.
48-L	1	4	5	6.2	15.4	78.4	1,835	Fusion started at 1,790°, complete at 1,835°	Principal phases are chrysoberyl and the "ternary" compound, with spinel rare.

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[a] The term "complete fusion" means that the pyramidal specimen had fused sufficiently to flow into a flat button shape, and does not necessarily connote that the mixture had completely liquefied.

[b] This possible ternary compound is uniaxial−, or has very small 2V; approx. indices of refraction ω-1.722, ϵ-1.715; twinning common with optic axis perpendicular to twinning.

tion of the diagram consists of the subordinate ternary system MgO-BeO-spinel with a ternary eutectic at 1,640° C and, by weight, approximately 44.4 percent of MgO, 27.5 percent of BeO, and 28.1 percent of Al_2O_3 (mole ratio $4MgO{:}4BeO{:}Al_2O_3$). This is supported by X-ray patterns of the mole compositions $4MgO{:}4BeO{:}Al_2O_3$ and $4MgO{:}16BeO{:}Al_2O_3$, which had been heated at 1,710° and 1,650° C, respectively. These patterns contained only the lines for periclase, bromellite, and spinel. However, a ternary compound may be the primary phase in a small portion of the system. Subordinate systems, if any, in the remainder of the diagram are obscured by solid-solution areas and by this ternary compound, which will be discussed further in connection with the fields of stability.

(a) FIELDS OF STABILITY

Results of fusion-point and softening-range observations, and petrographic and X-ray analyses of typical heated specimens, are summarized in table 4. These results are the basis for the location of field boundaries, as given in figure 6. Duplicate determinations were made whenever necessary, but the only tests reported in the table are those judged as typical or representative of best data. The values are not conclusive. In several instances it is obvious that equilibrium had not been reached, and the slow cooling in the furnace may have often destroyed any evidence of phases present at the liquidus.

It is believed that the primary field of MgO is substantially as shown, and that the field of BeO must be limited in part very nearly as shown by its boundaries with the MgO and $MgAl_2O_4$ fields. There is considerable doubt regarding the boundaries of the fields for $BeAl_2O_4$, Al_2O_3, and the postulated ternary compound.

It seems reasonably certain that a ternary compound is the primary phase in a small field approximately as indicated, that it melts incongruently, and that the compound composition is (in mole ratio) at or near $MgO{:}BeO{:}2Al_2O_3$. This supposedly ternary compound either is uniaxial or has a very small optic angle. The character is negative, twinning is common with the optic axis perpendicular to the twinning, and the indices of refraction are ω-1.722 to 1.725, ϵ-1.715 to 1.718. X-ray patterns for this phase in compositions $MgO{:}2BeO{:}2Al_2O_3$, $MgO{:}BeO{:}2Al_2O_3$, $MgO{:}2BeO{:}3Al_2O_3$, and $MgO{:}2BeO{:}Al_2O_3$ showed no significant shift from the lines given in table 5, such as would result if the phase were the result of solid solution. Nevertheless, the possibility remains that it is a solid solution. If the high indices of refraction of compositions along the spinel-chrysoberyl join are compared, there is apparently an almost continuous variation from chrysoberyl, through the new phase, to spinel. Also, as the crystal structures of $BeAl_2O_4$ and $MgAl_2O_4$ are similar, solid solution may be expected in this area.

The optical evidence that the field ascribed to the ternary compound extends into the MgO-BeO-spinel system is contradictory (test 198, table 4), but results of the fusion tests contain some evidence that the system BeO-spinel is not a simple one. Both $MgO{:}3BeO{:}Al_2O_3$ and $MgO{:}1.5BeO{:}Al_2O_3$ fused sharply at about 1,745° C, whereas the composition $MgO{:}2BeO{:}Al_2O_3$ fused from 10° to 15° C higher. This relatively greater refractoriness of the 1:2:1 composition was not observed for these compositions when heated at lower temperatures (e. g. 1,700° C).

TABLE 5.—*Diffraction data from patterns for the dominant phase in compositions* $MgO:BeO:2Al_2O_3$ and $MgO:2BeO:2Al_2O_3$, *tests 352 and 355, table 4 (by H. F McMurdie)*

[VS=very strong, S=strong, M=medium, W=weak, VW=very weak]

Estimated intensity of lines	*d*	Estimated intensity of lines	*d*
	A		*A*
M	4.56	VS	2.05
M	4.22	VW	1.931
VW	4.05	M	1.875
W	3.25	VW	1.766
W	3.12	VW	1.717
VW	2.98	M	1.618
W	2.83	M	1.596
M	2.66	W	1.568
VW	2.56	W	1.535
VW	2.51	S	1.482
VS	2.40	VW	1.463
W	2.34	M	1.438
S	2.27	S	1.415
VW	2.18	M	1.362
M	2.09	W	1.322

(b) CERAMIC BODIES

The preparation of specimens for mechanical and electrical tests was limited to compositions that could be heated through a range of at least 25 deg C to produce a vitreous structure. Such compositions, when prepared and heated by the methods used in this study, are confined to the area lying between the BeO apex and the solid curved line in figure 6. Specimens of compositions in the remainder of the diagram either did not vitrify at the temperatures to which they were subjected, or passed from a porous (or underfired) condition to one in which they deformed under their own weight through a very short temperature range.[7] Vitrification ranges for the compositions prepared as test specimens are given in table 6. Although many of these compositions have long vitrification ranges, the shrinkage values indicate that the optimum maturing temperature producing the maximum density is in all cases in the upper portion of the range.

Specimens of six compositions were tested for strength in compression and for dielectric properties. Average values are given in table 7. From the data presented in table 2, and from the results for the specimens from tests 132–L and 181–L (table 7), it is evident that values obtained by crushing the pieces between porcelain blocks did not represent their full resistance to failure. It is unfortunate that the advantage of using cold-rolled steel was not discovered earlier in the investigation, and time did not permit repeating the work.

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[7] It should be noted that ternary compositions containing more than 80 to 90 percent of Al_2O_3 are vitrifiable according to patent literature [18] but they were not prepared in this investigation.

TABLE 6.—*Temperature range in which* MgO-BeO-Al_2O_3 *specimens attained an absorption of less than 0.1 percent, and resultant linear shrinkage*

Composition (mole)			Vitrification range		Shrinkage range
MgO	BeO	Al_2O_3	1[a]	2[b]	
			°*C*	°*C*	%
1	24	1	1,600 to 1,725	[c] 1,625	15.5 to 17.6
1	16	1	1,600 to 1,725	None	15.5 to 16.5
1	8	1	1,625 to 1,725	------do------	13.6 to 14.4
1	4	1	1,680 to 1,725	--------------	11.2 to 12.0
1	2	1	[d] 1,650	None	9.7
4	96	1	1,500 to 1,635	1,500 to 1,625	17.9 to 20.0
4	48	1	1,500 to 1,635	1,500 to 1,625	16.8 to 19.4
4	24	1	1,600 to 1,630	1,560 to 1,625	14.4 to 20.5
4	16	1	[c] 1,630	1,560 to 1,600	15.5 to 20.0
4	8	1	None	1,560 to 1,600	21.6 to 22.2
2	4	1	[e] 1,600	--------------	13.0

[a] Specimens made with fused magnesia and commercial alumina.
[b] Specimens made with calcined magnesia and laboratory prepared alumina.
[c] Not vitreous when heated 25° C above or below this temperature.
[d] Overfired at 1,700° C.
[e] Partly fused at 1,650° C.

The dielectric tests show interestingly low power losses in some cases. Values for electrical resistivity (T_e value) and relative thermal conductivity are given in table 8. The trend is for both electrical resistivity and thermal conductivity to increase with increase in the BeO content. Values for the specimens from test 27–L indicate that electrical resistivity may be relatively greater for a composition when heated above the vitrification range, and having an "overfired" and porous structure, than for comparable pieces heated to vitrification. Compared with conventional feldspathic porcelains [19, 20], the thermal expansion is high for all of the compositions tested (table 9).

TABLE 7.—*Resistance to crushing, and dielectric properties, of typical compositions in the* MgO-BeO-Al_2O_3 *system*

[Specimens made with fused magnesia and commercial alumina]

Specimen from test No.	Composition (mole)			Matured at—	Number of specimens	Absorption	Compressive strength [a]	Number of specimens	Absorption	Dielectric properties at 100 kc/s [b]	
	MgO	BeO	Al_2O_3							Constant	Loss angle
				°*C*		%	*lb/in.*^{2}		%	*K*	tan δ
84–L	1	24	1	1,725	------	------	------	3	0.04	6.8	0.002
132–L	1	24	1	1,725	3	0.01	169,000	------	------	------	------
160–L	1	24	1	1,600	------	------	------	1	.01	6.7	.0006
181–L	1	24	1	1,650	3	.00	[a] 286,000	2	.00	6.9	.004
85–L	1	8	1	1,725	3	.03	152,000	2	.04	6.8	.001
86–L 94–L }	1	4	1	1,725	3	.04	142,000	2	.07	6.5	.002
87–L	4	96	1	1,630	3	.06	105,000	------	------	------	------
91–L	4	96	1	1,635	3	.02	144,000	2	.04	6.6	.003
88–L	4	24	1	1,630	2	.06	137,000	------	------	------	------
95–L	4	24	1	1,630	3	.04	129,000	2	.04	6.9	.070
93–L	4	8	1	1,635	3	.24	136,000	2	.34	7.7	.021

[a] The contact blocks between the specimens and the press platens were porcelain in all cases except for specimens from test 181–L, in which case cold-rolled steel was used (see table 2).
[b] The dielectric values were determined by C. M. Sparks and A. H. Scott.

TABLE 8.—*Electrical resistivity (T_e value) and relative thermal conductivity of compositions in the* MgO-BeO-Al_2O_3 *system (each value represents one specimen)*

[Specimens made with fused magnesia and commercial alumina]

Specimen from test No.	Composition (mole)			Matured at—	Absorption	Electrical resistivity[a] (T_e value)	Absorption	Thermal conductivity[b]
	MgO	BeO	Al_2O_3					
				° C	%	° C.	%	
76-L	4	96	1	1,635	0.01	1,190	0.01	11
194	4	96	1	1,655	.06	1,195		
80-L	4	48	1	1,630	.09	1,180	.00	11
179	4	48	1	1,655	.01	1,178		
78-L	4	24	1	1,630	.01	1,161	.01	12.5
156	4	24	1	1,645	.30	1,166		
78-L	4	16	1	1,630	.03	1,156	.03	9
37-L	4	16	1	1,660	.10	1,190		
76-L	4	16	1	1,635	.02	1,161		
213	4	8	1	1,625	.30	1,110	.32	7
217	4	8	1	1,640	.26	1,127		
218	4	8	1	1,630	.31	1,106		
76-L	4	4	1	1,635	.19	1,140	.19	3
139	4	4	1	1,640	.40	1,142		
217	4	4	1	1,640	.35	1,127		
218	4	4	1	1,630	.35	1,106		
241	1	24	1	1,720			.01	11
82-L	1	24	1	1,725	.01	1,137	.01	9
27-L	1	24	1	1,775	1.50	1,210		
159	1	24	1	1,720	0.10	1,150		
61-L	1	16	1	1,735			.01	8
82-L	1	16	1	1,725	.01	1,136	.01	6
27-L	1	16	1	1,775	1.50	1,200		
152	1	16	1	1,740	0.70	1,131		
158	1	16	1	1,720	.06	1,185		
82-L	1	8	1	1,725	.02	1,125	.02	5
167	1	8	1	1,720	.06	1,155		
86-L	1	4	1	1,720	.03	1,124	.03	4
82-L	1	4	1	1,725	.04	1,134		

[a] The T_e value for electrical resistivity is the temperature at which, by calculation based on test values, a 1-cm cube of the material has a resistance of 1 megohm. The values were obtained by E. N. Bunting.

[b] These values are the reciprocal, multiplied by 100, of the temperature drop through a 0.5-in. height of specimen approximately ½ in. in diameter. The values were determined by E. N. Bunting.

In general, it may be said that compositions over a wide range in the MgO-BeO-Al_2O_3 system show interesting possibilities as vitreous ceramic bodies. Specimens developed very high strength in compression and, even when tested under conditions that were not the most advantageous, the values ranged from 105,000 to 169,000 lb/in.^{2} This compares very favorably, for example, with values obtained for commercially prepared unglazed specimens of high-tension insulator porcelains [20], which ranged from 27,000 to 88,000 lb/in.^{2} in compressive strength. The electrical resistivities compare favorably with those for various types of spark-plug insulator compositions which, as published by Riddle [21], range in *Te* value from 632° to 1,066° C. The dielectric properties are good, and the thermal conductivity will range from about that of a commercial high-alumina body to practically the conductivity of a vitreous specimen of BeO, which is three to four times greater than that of the alumina body.

TABLE 9.—*Linear thermal expansion data*

Specimen from test No.	Composition (mole)					Coefficient×10^6										Expansion to 1,000° C
	MgO	BeO	Al_2O_3	ThO_2	ZrO_2	Room temp. to 100° C	100° to 200°	200° to 300°	300° to 400°	400° to 500°	500° to 600°	600° to 700°	700° to 800°	800° to 900°	900° to 1,000°	%
139	8	4	1	------	------	7.0	8.7	9.6	8.2	10.5	11.1	10.4	10.8	9.4	9.3	0.930
27-L	4	96	1	------	------	5.3	7.0	7.7	8.7	9.6	9.2	10.0	10.3	9.2	------	[a].755
40-L	4	4	1	------	------	5.6	6.7	7.8	8.8	9.4	10.5	8.5	10.1	11.0	9.5	.851
27-L	1	16	1	------	------	5.2	6.7	7.9	8.7	9.5	9.8	9.8	10.5	10.9	9.9	.876
137	1	4	1	------	------	5.4	6.7	8.5	8.1	9.8	9.7	9.3	9.4	9.5	9.1	.843
54-L	1	1	4	------	------	5.2	7.0	8.0	8.1	9.6	8.8	8.7	9.2	10.0	9.5	.828
182-L	------	48	1	1	------	4.4	7.0	6.9	7.8	9.3	9.7	9.0	10.0	9.6	------	[a].726
182-L	------	12	1	1	------	5.4	7.3	8.2	8.7	9.4	9.7	10.1	10.7	10.4	9.1	.875
182-L	------	160	2	1	------	4.7	6.7	8.2	7.9	7.9	9.7	10.0	10.4	10.2	------	[a].745
182-L	------	24	2	1	------	5.3	7.1	8.1	8.5	9.4	9.6	10.5	9.7	11.0	9.9	.876
182-L	------	48	4	1	------	4.8	7.1	8.0	8.6	9.8	9.5	9.7	11.9	10.0	------	[a].780
182-L	------	18	4	1	------	5.2	7.0	7.8	8.5	9.5	9.0	9.0	10.5	9.7	9.7	.846
171-L	------	48	10	1	------	4.8	6.9	8.1	8.2	8.6	8.6	9.2	10.1	8.6	------	[a].714
278	------	4	4	1	------	5.4	7.1	6.8	8.5	9.1	9.1	8.9	9.8	9.3	9.4	.819
173-L	------	8	1	------	2	5.2	6.9	7.8	8.2	9.0	8.9	8.9	9.3	9.7	8.3	.810

[a] Expansion to 900° only.

(c) REACTION WITH WATER

A limited number of pieces were tested as indicated in table 10 in order to obtain some relative numerical values for the resistance of nonvitreous specimens to the action of water. The data show that some "hydrolysis" (weight retained after drying at 110° C) and solution (loss in weight after heating at 800° C) had resulted. Although not serious in most cases, it was thought sufficient to justify the procedure of boiling in CCl_4.

TABLE 10—*Effect of boiling fired specimens of* MgO-BeO-Al_2O_3 *compositions in water*

Specimen from test No.	Composition (mole)			Absorption [a]	Specimens boiled in water for 5 hr	
	MgO	BeO	Al_2O_3	%	Gain in weight after redrying at 110° C %	Change in weight after redrying at 800° C %
37-L	4	96	1	1.35	0.025	−0.008
166	4	96	1	0.93	.12	−.013
166	4	96	1	.15	.04	−.021
37-L	4	48	1	1.44	.05	−.013
37-L	4	16	1	0.10	.005	−.018
156	4	24	1	.34	.06	−.03
36-L	4	8	1	(b)	----------	(c)
154	4	8	1	1.14	.23	−.01
40-L	4	8	1	1.02	.28	−.05
40-L	4	4	1	0.23	.11	+.02
40-L	4	2	1	3.13	1.10	+.05

[a] Based on weight of specimen after boiling and after redrying at 800° C

[b] Porous.

[c] Disintegrated.

5. THE SYSTEM CaO-BeO-Al_2O_3

The subordinate binary system CaO-BeO is apparently free from solid solution. Wartenburg and coworkers [16] reported the eutectic at about 1,450° C and 50 wt percent of CaO. In this investigation, the eutectic was found at 1,405° C and approximately 65 wt percent of CaO. Compositions between CaO and CaO:BeO (or 100 percent and 69.2 percent of CaO by weight) contained CaO in well-defined cubes of refractive index 1.84 as the primary phase. The matrix was isotropic with a refractive index of 1.64. Compositions between CaO:1.5BeO and BeO (or 59.9 percent and zero percent of CaO by weight) showed well-crystallized BeO as the primary phase. The addition of 1 percent by weight of CaO to BeO made it possible to obtain nonabsorbent specimens as low as 1,375° C and the vitrification range extended to over 1,500° C.

Only a relatively small number of bodies in the ternary system were investigated. The results indicate that some advantage would be gained over the corresponding MgO-BeO-Al_2O_3 system so far as the temperatures required for vitrification are concerned. For example, five ternary compositions containing 70 percent or more of BeO, and from 5 to 20 percent of CaO, vitrified between 1,400° and 1,500° C. In general, the texture was coarsely crystalline, and no tests of mechanical strength or thermal and electrical properties were made.

6. THE SYSTEM BaO-BeO

Specimens ranging in mole composition from BaO:BeO to BaO:12BeO (85.97 percent to 33.81 percent by weight of BaO) were heated at 1,170°, 1,250°, 1,300°, and 1,400° C. They were placed on BeO in the kiln because the first trials had shown reaction with platinum. At 1,170° C the 1:1 mixture fused partly and the 1:2 mixture became sintered. At 1,400°, the 1:1 and 1:2 mixtures fused completely, the 1:3 was bloated, and the 1:6 and 1:12 specimens appeared vitreous, coarse-grained, and were medium gray in color. BeO crystals, and the absence of free BaO, characterized all the heated samples. An unidentified phase at the high-BaO end of the series is probably orthorhombic, with $2V=90°$, and the refractive index is slightly above 1.77. At the high-BeO end another unidentified phase appears to be monoclinic. It is biaxial negative, $2V=75°$, and the refractive indices are $\gamma=1.77$, $\beta=1.768$(?), $\alpha=1.764$. Extinction is oblique, and its two cleavages are at an angle of 78°. This system may be complicated by a low-temperature eutectic between BaO and $BaCO_3$ [24].

The preparation of specimens for mechanical or electrical tests was not attempted.

7. THE SYSTEM BeO-Al_2O_3-ThO_2

This is a distinctly high-temperature system. Thoria is described [22] as fusing at about 3,000° C. It is a cubic compound with the very high refractive index of 2.20±, as given by Larsen [23]. In the specimens examined it occurred generally as rounded or angular grains, as rods, or as spherules. It was not observed in the cubic habit. The other end members of the system, BeO and Al_2O_3, fuse at about 2,520° C [16] and 2,015° ±15° C [12], respectively. The lowest liquidus point in the ThO_2-BeO system is reported [16] to be at 2,200° C and about 20 percent by weight of BeO. In this study, the lowest melting eutectic in the BeO-Al_2O_3 system was placed at 1,865° C (fig. 6).

According to the results of this investigation, the Al_2O_3-ThO_2 eutectic is at 1,910° C and 60.7 wt percent of Al_2O_3 or, in mole ratio, at $4Al_2O_3$:ThO_2, which is in good agreement with the findings of Wartenburg and Reusch [15]. The location of the eutectic (fig. 7) is based on fusion tests entirely, as microscopic examinations (table 11) showed no differences in texture that were useful for that purpose. The intergrowth texture in fused specimens of Al_2O_3:$2ThO_2$, Al_2O_3:ThO_2, $2Al_2O_3$:ThO_2, and $3Al_2O_3$:ThO_2 may result from solid solution at high temperatures, and unmixing during cooling, but the evidence is not conclusive.

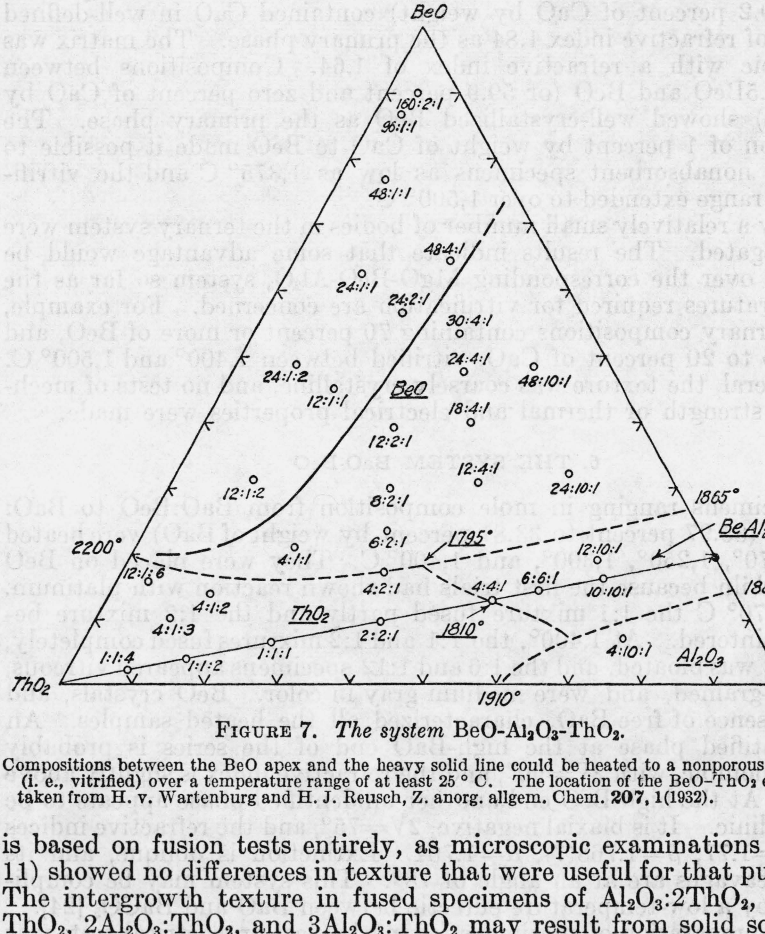

FIGURE 7. *The system* BeO-Al_2O_3-ThO_2.

Compositions between the BeO apex and the heavy solid line could be heated to a nonporous structure (i. e., vitrified) over a temperature range of at least 25 ° C. The location of the BeO-ThO_2 eutectic is taken from H. v. Wartenburg and H. J. Reusch, Z. anorg. allgem. Chem. **207**, 1(1932).

The thermal reactions in most of the mixtures of ThO_2 and Al_2O_3, and also in mixtures along the chrysoberyl-thoria tie-line, are characterized by the formation of very low viscosity liquids, as evidenced (1) by the rapidity with which softening and flow progressed when the solidus temperature was exceeded, (2) by the fact that beginning of fusion was clearly defined and was within a few degrees of the pertinent eutectic temperature, and (3) by the literal disappearance of Al_2O_3 test pieces into the pores of the ThO_2 shapes upon which the pieces had been supported whenever they were heated above the Al_2O_3-ThO_2 eutectic temperature.

The results of fusion tests and microscopic examinations agree with the assumption that a simple system exists between chrysoberyl ($BeAl_2O_4$) and thoria, with limited solid solution at some higher temperature, as indicated by "exsolution" texture. Nearly the entire ternary system is therefore, on a weight basis, occupied by the subordinate system BeO-$BeAl_2O_4$-ThO_2. Compositions in the $BeAl_2O_4$-ThO_2 system (fig. 7), varying in ThO_2 content from about 25 to 80 percent, all fused within a range of ±10 deg C. The eutectic in this system was placed at 1,810° C and $4BeO:4Al_2O_3:ThO_2$, partly because of the proximity of this composition to the Al_2O_3-ThO_2 eutectic, partly because of an apparently higher liquidus on either side, and in spite of the sharp fusion at 1,800° to 1,805° of the compositions $BeO:Al_2O_3:2ThO_2$ and $BeO:Al_2O_3:ThO_2$. There is no logical explanation from the data for this fusion behavior of the 1:1:2 and 1:1:1 mixtures. The lowest ternary eutectic is believed to be at 1,795° C and near the mole composition $4BeO:2Al_2O_3:ThO_2$.

(a) FIELDS OF STABILITY

The fields of stability of the primary phases and the critical temperatures are believed to be very nearly as shown in figure 7, based on the information given in table 11. There appears to be limited solid solution between ThO_2 and $BeAl_2O_4$, as mentioned previously, and from the chrysoberyl end of this binary system the solid-solution seems to extend toward the Al_2O_3 apex so as to include the mole composition $4BeO:10Al_2O_3:ThO_2$.

(b) CERAMIC BODIES

It is possible to vitrify most of the compositions in the BeO field of the BeO-$BeAl_2O_4$-ThO_2 system, but the temperature range through which a nonporous structure can be obtained is greatest near the BeO apex. This range decreases rapidly with increase in alumina content and more gradually with increase in thoria content. Only those ternary compositions between the BeO apex and the solid curved line in figure 7 were vitrified over a range of at least 25 deg C. The optimum temperature interval in which to produce nonporous specimens was from 1,600° to 1,750° C. Several compositions on the opposite side of the solid curved line were vitrified by heating at 1,700° C and three (1:1:2, 4:4:1 and 12:10:1) by heating at 1,750° C. No significant differences in vitrification behavior were observed between specimens made with calcined thoria and those made with fused thoria.

Good strength in compression was obtained with the mole compositions $160BeO:2Al_2O_3:ThO_2$ and $48BeO:Al_2O_3:ThO_2$. The former, when matured at 1,725° C, and the latter at 1,750° C, showed less than 0.02-percent absorption. The specimens were crushed between cold-rolled steel blocks and gave average values of 244,000 lb/in.^{2} for the 160:2:1 mix and 279,000 lb/in.^{2} for the 48:1:1 mix. Minimum values for individual specimens of the two compositions were 240,000 and 274,000 lb/in.^{2}, respectively. These bodies also had promising power-loss values of less than 0.01 percent at 100 kc/s, and the K value ranged between 7 and 8. Coefficients of linear thermal expansion for the 160:2:1 mix, and for other compositions in this system, are given in table 9. Values for electrical resistivity and thermal conductivity are given in table 12.

TABLE 11.—*Results of fusion tests and softening range determinations, and X-ray and microscopical examinations, of the specimens in the system* $BeO-Al_2O_3-ThO_2$

Test No.	Composition						Heated at (max).—	Effect of heating (temperatures in degrees centegrade)	Results of X-ray and microscopical examinations. (Specimens examined were not quenched and the phases observed may not be those in equilibrium at the maximum temperature of heating or at the liquidus)
	Mole			Weight					
	BeO	Al_2O_3	ThO_2	BeO	Al_2O_3	ThO_2			
				%	%	%	°C		
363	------	1	2	------	16.15	83.75	1,925	Fusion incomplete; started at 1,910°	Thoria as rounded grains is the major constituent. Remainder is interstitial alumina, angular ThO_2, and ThO_2 in intergrowth texture.
374	------	1	1	------	27.80	72.20	1,915	Fusion complete [a]; started at 1,910°	Thoria as rounded grains and in intergrowth texture. Alumina is interstitial to the thoria.
365	------	2	1	------	43.55	56.45	1,920	Fusion complete; started at 1,905°	Thoria occurs as rounded grains and intergrowth texture in a matrix of alumina.
367	------	3	1	------	53.65	46.35	1,915	Fusion complete; started at 1,910°	Do.
366	------	4	1	------	60.70	39.30	1,910	Complete fusion at this temperature	No intergrowth texture. ThO_2 and Al_2O_3 present as irregular and as rounded grains.
364	------	6	1	------	69.85	30.15	1,915	Fusion complete; started at 1,910°	Alumina in large angular grains and thoria in relatively small angular grains.
376	------	10	1	------	79.40	20.60	1,935	Fusion far from complete; started at 1,920°	
389	12	1	6	15.10	5.13	79.77	1,935	Vitreous. Little if any softening.	
370	1	1	4	2.1	8.6	89.3	1,900	Fusion incomplete; started at 1,805°	About 95 percent of thoria, and 5 percent of chrysoberyl containing thoria in intergrowth texture.
446	4	1	3	10.05	10.25	79.70	1,875	Fusion incomplete; started at 1,820°.	
442	24	1	2	48.8	8.3	42.9	1,925	No softening	BeO as blocky grains 20 to 30 microns in diameter, thoria as angular fragments 1 to 20 microns in size, and chrysoberyl very rare.
381	12	1	2	32.25	10.95	56.80	1,925	Fusion far from complete; started at 1,865°	BeO and ThO_2, mostly as blocky and irregular grains. No $BeAl_2O_4$ noted.
382	4	1	2	13.70	13.95	72.35	1,875	Fusion incomplete; started at 1,835°	Rounded grains of ThO_2 are surrounded by a very fine-grained intergrowth texture of ThO_2 in BeO. Angular fragments of ThO_2, and a few grains of $BeAl_2O_4$ also present.
359	1	1	2	3.80	15.55	80.65	1,805	Fused quickly at 1,800°	Thoria, both in rounded grains and intergrowth texture, and interstitial chrysoberyl.
297–L	96	1	1	86.80	3.65	9.55	1,800	No softening.	
312–L	48	1	1	76.6	6.5	16.9	1,800	do	
388	24	1	1	62.15	10.55	27.30	1,935	Fusion far from complete	Only beryllia and thoria were identified.
368	12	1	1	45.1	15.3	39.6	1,905	Fusion incomplete; started at about 1,825°	BeO as prismatic or lath-shaped crystals, in some cases containing rounded grains of thoria. Thoria in rounded and angular grains.
384	4	1	1	21.45	21.85	56.70	1,875	Fusion well advanced; started at 1,840°	BeO interstitial to rounded and angular grains of ThO_2. Large crystals of BeO at the base of the specimen.

358	1	1	1	6.40	26.05	67.55	1,805	Complete fusion between 1,800° and 1,805°	Thoria in a matrix of chrysoberyl. Considerable intergrowth texture. X-ray pattern contains lines for ThO_2 and $BeAl_2O_4$.
313	160	2	1	90.00	4.35	5.65	1,850	No softening.	
377	24	2	1	56.2	19.1	24.7	1,900	Fusion far from complete; started at 1,835°	BeO in lath-shaped and irregular grains. ThO_2 in rounded grains, both free and as inclusions in BeO. Occasional grains of chrysoberyl. X-ray pattern has lines for BeO and ThO_2 only.
386	12	2	1	39.1	26.5	34.4	1,860	Fusion incomplete; started at 1,845°	Largely ThO_2 as rounded grains, and as both coarse and fine intergrowth with BeO. No $BeAl_2O_4$ identified.
444	8	2	1	30.0	30.5	39.5	1,875	Fusion incomplete; started at 1,820°.	
387	6	2	1	24.3	33.0	42.7	1,845	Fusion not complete; softened rapidly above 1,835°	BeO is interstitial to ThO_2, which occurs as rounded grains and in intergrowth texture.
391	4	2	1	17.6	35.9	46.5	1,805	Fusion almost complete, advanced rapidly above 1795°	ThO_2, BeO, and $BeAl_2O_4$ in coarse and fine intergrowth texture.
331	2	2	1	9.7	39.1	51.2	1,820	Completely fused; started at 1,810°	Characterized by large twinned crystals of chrysoberyl with thoria in parallel arrangement of minute rods.
380	48	4	1	64.1	21.8	14.1	1,920	Incipient fusion	Beryllia in blocky grains containing inclusions of thoria. No chrysoberyl identified.
176–L	30	4	1	52.80	28.65	18.55	1,750	No softening.	
379	24	4	1	47.20	32.05	20.75	1,925	Fusion well advanced; started about 1,850°	Very similar to specimen from test 377.
195–L	18	4	1	40.10	36.35	23.55	1,750	No softening.	
357	12	4	1	30.90	41.95	27.15	1,905	Fusion well advanced; started at 1,870°	Principal phases are BeO and $BeAl_2O_4$. ThO_2 occurs as parallel arranged inclusions in the BeO and as rounded particles in the $BeAl_2O_4$.
207–L	4	4	1	12.95	52.85	34.20	1,810	Fused sharply at 1,810°	Chrysoberyl as blocky crystals with ThO_2 inclusions in various forms (rods, amoeboid and rounded grains.) Exsolution texture is present in about one-third of the $BeAl_2O_4$.
353	6	6	1	14.65	59.60	25.75	1,815	Complete fusion between 1,810° and 1,815°	Some chrysoberyl in large plates. Otherwise similar to specimen from test 207–L.
176–L	48	10	1	48.35	41.00	10.65	1,750	No softening.	
449	24	10	1	31.9	54.1	14.0	1,900	Fusion incomplete; started at 1,810°	Large (0.5 to 1.0 mm) crystals of $BeAl_2O_4$. ThO_2 occurs as rounded parallel rods and amoeboid grains in the chrysoberyl. BeO present, but rare.
448	12	10	1	19.0	64.3	16.7	1,840	Fusion complete; started at 1,800°	Chrystal phases similar to specimen from test 449. X-ray pattern shows lines for $BeAl_2O_4$ and ThO_2.
354	10	10	1	16.33	66.43	17.24	1,850	Fusion complete; started at 1,825°	Some large plates of chrysoberyl but all $BeAl_2O_4$ crystals contain ThO_2 in exsolution texture. May be in a solid-solution area.
447	4	10	1	7.2	73.7	19.1	1,860	Fusion far from complete; started at 1,820°	Large platy crystals of $BeAl_2O_4$ containing amoeboid grains of ThO_2 in parallel orientation. Main portion of sample is chrysoberyl and thoria in equigranular formation. No corundum could be found. The X-ray pattern also contains no lines for Al_2O_3 but shows a slight shift in the lines for chrysoberyl. May be in a solid-solution area.

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[a] The term "complete fusion" means that the pyramidal specimen had fused sufficiently to flow into a flat button shape, and does not necessarily connote that the mixture had completely liquefied.

TABLE 12.—*Absorption, electrical resistivity (T_e value) and relative thermal conductivity of compositions in the system* BeO-Al_2O_3-ThO_2 *(each value represents 1 specimen)*

Specimen from test No.	Composition (mole)			Matured at—	Absorption	Electrical resistivity [a] (T_e value)	Thermal conductivity [b]
	BeO	Al_2O_3	ThO_2				
				°C	*Percent*	*°C*	
320-L	12	1	2	1,700	0.00	---	12
294-L	12	1	2	1,700	.02	767	---
300-L	24	1	1	1,750	.02	---	11
233-L	24	1	1	1,650	.01	945	---
191-L	12	1	1	1,700	.00	---	14
195-L	12	1	1	1,750	.01	910	---
254-L	160	2	1	1,650	.00	---	25
197-L	24	2	1	1,675	.00	---	5
175-L	24	2	1	1,700	.01	1,005	---
175-L	24	2	1	1,700	.01	1,076	---
320-L	12	4	1	1,700	.00	---	4
191-L	12	4	1	1,700	.01	994	---
175-L	48	10	1	1,700	.11	---	6
191-L	48	10	1	1,700	.02	1,135	---
320-L	24	10	1	1,700	.00	---	10
191-L	24	10	1	1,700	.02	1,057	---
453	12	10	1	1,750	.01	---	4
195-L	12	10	1	1,750	.01	968	---
258	---	---	1	2,040	1.90	490	---

[a] The T_e value for electrical resistivity is the termperature at which by calculation based on test values, a 1-cm cube of the material has a resistance of 1 megohm. These values were obtained by E. N. Bunting.

[b] These values are the reciprocal, multiplied by 100, of the temperature drop through a 0.5-in. height of specimen approximately 0.5 in. in diameter, and were determined by E. N. Bunting.

8. THE SYSTEM BeO-Al_2O_3-ZrO_2

The phase relations in this system (fig. 8) are, in all probability, much like those in the system BeO-Al_2O_3-ThO_2. The evidence points to a simple binary relation between chrysoberyl and zirconia, with the possibility of limited solid solution (table 13). As a generalization, one can say that the beginning of fusion of the ternary mixtures will average about 50 deg C lower than for corresponding mixtures in the BeO-Al_2O_3-ThO_2 system, but the binary eutectics of the end members are about the same in the two systems. The eutectic between Al_2O_3 and ZrO_2 at about 50 mole percent, or 55 wt percent, of ZrO_2 has been reported at 1,920° C [25] and at 1,900° C [15]. In this study, fusion was observed at 1,885° C. For the system BeO-ZrO_2, a compound ($3BeO:2ZrO_2$) and two eutectics were reported in 1930 [26], but a year later a single eutectic at about 75 wt percent of ZrO_2 and 2,240° C was reported [27]. In the present study, no evidence was found of a compound between BeO and ZrO_2.

(a) FIELDS OF STABILITY

The fusion data in table 13 indicate that the various stability fields are as presented in figure 8. Both the ternary eutectic for beryllia, zirconia, and chrysoberyl, and the binary eutectic for zirconia and chrysoberyl, are believed to be very nearly as shown. These points, together with the eutectics in the binary systems of the end members, serve to approximate the location of the field boundaries. The least certain is the location of the boundary between the fields of chrysoberyl and Al_2O_3.

The dotted line (fig. 8) encloses a group of compositions, all of which contained an exsolution texture after having been heated at or near the fusion temperature. This exsolution texture is evidence of some degree of solid solution. Within this area, ZrO_2 occurs partly as rods or as amoeboid and graphic forms in chrysoberyl. Tetragonal zirconia in the exsolution texture may invert in part to the monoclinic form during cooling, and some amoeboid grains of tetragonal ZrO_2 contain lathlike crystals of lower refractive index and higher birefringence than the enclosing grains. This evidence is assumed to indicate that solid solution and exsolution occur within the range of temperatures in which tetragonal ZrO_2 is the stable phase, probably between 1,000° and 1,500° C [12].

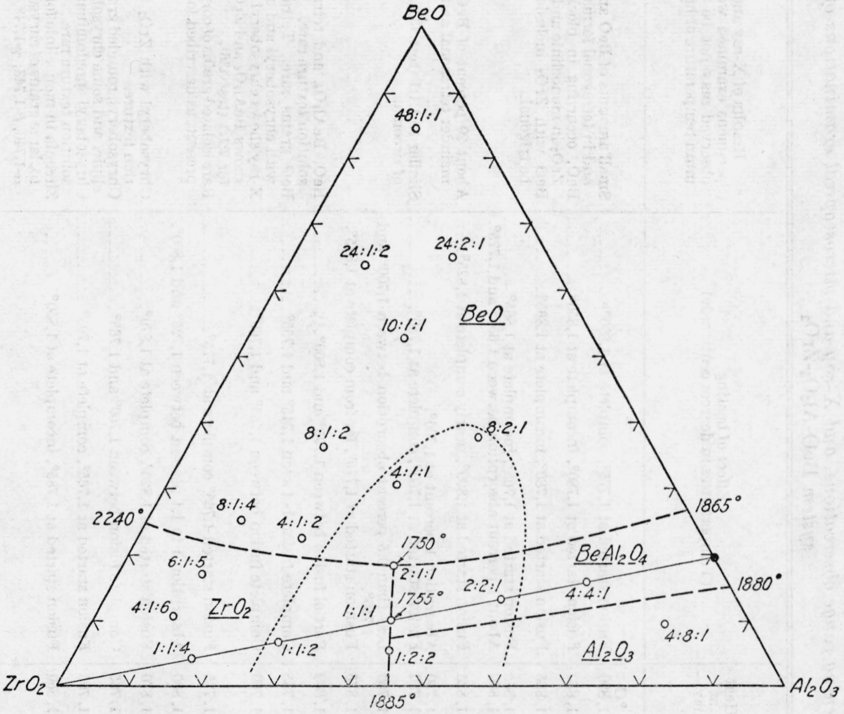

FIGURE 8. *The system* BeO-Al_2O_3-ZrO_2.

No composition in this system was vitrified. The location of the BeO-ZrO_2 eutectic is taken from H. v Wartenburg and W. Gurr, Z. anorg. allgem. Chem. **196**, 374 (1931).

(b) CERAMIC BODIES

No composition in this system became vitrified (i. e., had less than 0.1-percent absorption) at any of the temperatures to which it was heated. These temperatures ranged from 1,600° to 1,800° C. Only one composition, mole ratio $48BeO:Al_2O_3:ZrO_2$, attained an absorption of less than one-half percent (table 13). No specimens were prepared for mechanical strength or for electrical tests, but the thermal expansion data are given in table 9 for one specimen with an absorption of 1.4 percent. The T_e value for a specimen of ZrO_2, with an absorption of 2.3 percent after having been heated at 1,900° C, was 421, and the thermal conductivity value (see footnote "b", table 12) for the same specimen was 1.4.

TABLE 13.—*Results of fusion point and softening range observations, and X-ray and microscopical examinations of the tested specimens in the system* $BeO-Al_2O_3-ZrO_2$

Test No.	Composition						Heat at (max)—	Effect of heating (Temperatures in degrees centigrade)	Results of X-ray and microscopical examinations (Specimens examined were not quenched and the phases observed may not be those in equilibrium at the maximum temperature of heating or at the liquidus)
	Mole			Weight					
	BeO	Al_2O_3	ZrO_2	BeO	Al_2O_3	ZrO_2			
				%	%	%	°C		
432	4	1	6	10.6	10.8	78.6	1,890	Fusion started at 1,775°, complete at 1,890°[b]	Small amounts of BeO and of $BeAl_2O_4$. ZrO_2 in monoclinic and in tetragonal forms.
329	6	1	5	17.3	11.7	71.0	1,850	Fusion started at 1,780°, incomplete at 1,850°	BeO, occurring in blocky grains, is rare. Remainder is ZrO_2 in monoclinic and tetragonal forms.
439	8	1	4	25.2	12.8	62.0	1,865	Fusion started at 1,780°, incomplete at 1,865°	BeO with ZrO_2 inclusions. ZrO_2 is uniaxial (+?), may be trigonal.
429	1	1	4	4.0	16.5	79.5	1,865	Fusion started at 1,765°, incomplete at 1,865°	
([a])	24	1	2	63.3	10.7	26.0	1,800	About 1-percent absorption between 1,650° and 1,775°.	
336	8	1	2	36.5	18.5	45.0	1,825	Fusion started at 1,800°, nearly complete at 1,825°	About 20 percent of BeO in laths and irregular grains, remainder tetragonal and monoclinic ZrO_2.
([a])	4	1	2	22.3	22.7	55.0	1,750	Absorption 1 percent at 1,700°.	
431	1	1	2	6.7	27.3	66.0	1,780	Fusion started at 1,760°, complete at 1,780°	Similar to 1:1:1 (test 433), except for larger relative quantity of zirconia.
([a])	48	1	1	84.2	7.1	8.7	1,750	Less than 0.5 percent absorption between 1,700° and 1,750°.	
434	10	1	1	52.6	21.5	25.9	1,875	Fushion started at 1,775°, far from complete at 1,875°.	
332	4	1	1	30.7	31.4	37.9	1,800	Partial fusion between 1,795° and 1,800°	BeO, $BeAl_2O_4$, and tetragonal and monoclinic ZrO_2. Exsolution texture rare.
436	2	1	1	18.2	37.0	44.8	1,755	Complete fusion between 1,745° and 1,755°	BeO grains rare. Tetragonal ZrO_2 in exsolution texture with chrysoberyl and also as rounded monoclinic grains.
433	1	1	1	10.0	40.7	49.3	1,760	Complete fusion between 1,755° and 1,760°	X-ray shows chrysoberyl and monoclinic ZrO_2. Microscope shows $BeAl_2O_4$ and ZrO_2 present in texture, as described for 2:1:1 (test 436).
437	1	2	2	5.3	42.9	51.8	1,775	Fusion started 1,765° complete at 1,775°	Rare isolated grains of corundum. Chrysoberyl and zirconia present, as described for 2:1:1 (test 436).
([a])	24	2	1	64.8	22.0	13.2	1,800	Absorption 1 to 1.4 percent between 1,725° and 1,800°.	
337	8	2	1	38.0	38.7	23.3	1,870	Fusion started at 1,820°, complete at 1,870°	Chrysoberyl with ZrO_2 inclusions, BeO rare, some exsolution texture.
326	2	2	1	13.2	54.1	32.7	1,765	Complete fusion between 1,760° and 1,765°	Chrysoberyl, rounded grains of ZrO_2 which are mostly monoclinic, and some chrysoberyl-zirconia exsolution texture.
438	4	4	1	15.8	64.6	19.6	1,795	Fusion started at 1,765°, complete at 1,795°	Chrysoberyl predominant, ZrO_2 mostly monoclinic, exsolution texture rare.
435	4	8	1	9.6	78.5	11.9	1,850	Fusion started at 1,785°, incomplete at 1,850°	Zirconia in monoclinic form as inclusions in, and interstitial to, large grains of chrysoberyl which has refractive indices α-1,740, β-1.743, γ-1.748.

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[a] A series of tests were made to determine range of minimum absorption.

[b] The term "complete fusion" means that the pyramidal specimen had fused sufficiently to flow into a flat button shape, and does not necessarily connote that the mixture had

9. RESISTANCE TO ATTACK BY PbO

The results of a limited number of tests to determine relative resistance to the attack of PbO, and made as described in section III, are summarized in table 14. The tests show (a) that attack on specimens immersed in molten PbO is much greater than on specimens exposed to PbO vapor, (b) that attack at 1,100° C is much greater than at 1,000° C, and (c) that, of the specimens tested, the siliceous bodies were the least resistant and the "high BeO" compositions were the most resistant.

The relatively low resistance of siliceous bodies of the mullite type may be explained by the low-melting eutectics in the $PbO-Al_2O_3-SiO_2$ system, in which there are four eutectics within the range 694° to 704° C [28]. In the binary system Al_2O_3-PbO, a eutectic occurs at 865° C [28], which no doubt accounts for the appreciable solution of the Al_2O_3 specimen of 99.95-percent purity. No data are available for the system PbO-BeO.

TABLE 14.—*Resistance to attack by PbO liquid and vapor*

Composition and absorption	Treatment for 4 hr at 1,100° C, except as noted	Result
Commercial A, mullite type	In vapor [a]	1.1-percent weight loss.
Commercial B, mullite type	do [a]	0.3-percent weight loss.
	In vapor	7.4-percent weight loss.
Commercial B, high alumina	do	5.5-percent weight loss.
	Partly immersed	Severe attack; over-all weight loss 34 percent.
Commercial C, high alumina	In vapor	Negligible loss.
	Partly immersed	Very severe attack; over-all weight loss 52 percent.
Commercial D, zircon type	In vapor [a]	2.1-percent weight loss.
	In vapor	6.7 percent weight loss.
BeO. (Abs. 0.02 percent)	Partly immersed	Original 0.5-in. diameter of immersed portion reduced by 0.008 in.
99 percent BeO, 1 percent MgO by weight. (Abs. 0.02 percent).	In vapor	Color change to 1-mm depth. Weight loss, 1.2 percent.
Do	Partly immersed	Discernible, but slight attack on immersed portion.
99 percent BeO, 1 percent CaO, by weight. (Abs. 0.01 percent.)	do	Only 0.007-in. decrease in diameter, but microscope shows interstitial penetration of PbO throughout specimen.
MgO; porous	do	0.02-in. decrease in diameter; PbO penetrated throughout mass, and isolated grains show considerable attack.
Al_2O_3, 99.95-percent purity. (Abs. 0.07 percent.)	Immersed	Considerable attack; over-all weight loss 9.8 percent.
ThO_2. (Abs. 1.9 percent)	In vapor	0.02-percent weight loss.
Chrysoberyl. (Abs. 0.03 percent)	do	No weighable weight loss.
Chrysoberyl. (Abs. 0.06 percent)	Partly immersed	Superficially no attack but microscope shows PbO penetration to about 0.06 in. depth and also interstitial solution products.
$4MgO:96BeO:Al_2O_3$ (mole). (Abs. av. 0.04 percent.)	In vapor	Duplicate samples showed 0.5-percent increase in weight. The microscope shows intercrystalline boundary attack to a depth of about 0.12 in.
$MgO:16BeO:Al_2O_3$ (mole). (Abs. 0.03 percent).	do	Showed 0.3-percent gain in weight.
$MgO:16BeO:Al_2O_3$ (mole). (Abs. 0.01 percent.)	Partly immersed	0.4 percent weight loss.

[a] Held for 4 hours at 1,000° C.

10. EFFECTS OF AUXILIARY OXIDES

This phase of the investigation was undertaken for two reasons: First, the addition of minor quantities of one or more oxides to a binary or ternary composition might lower the temperature range or enhance the degree of vitrification with no appreciable loss in mechani-

Table 15.—*Effect of minor oxide additions on the linear shrinkage (shr.) and absorption (abs.) of several compositions in the systems* $BeO-Al_2O_3-ThO_2$ *and* $BeO-Al_2O_3-ZrO_2$

[Duplicate tests were made only when the values of the first test appeared inconsistent with other values of a series. The asterisk (*) following an absorption value indicates that the specimen was overfied as judged by its deformation, blistering, or freezing to the platinum-rhodium plate on which it had been heated]

Oxide added	Matured at—	Base composition (mole)																	
		$24BeO:Al_2O_3:ThO_2$ [a]						$96BeO: Al_2O_3: ThO_2$ [a]						$160BeO: 2Al_2O_3: ThO_2$ [b]					
		Percentage by weight of oxide added to base composition																	
		8		4		2		8		4		2		8		4		2	
		Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.
	° *C*	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
CaO	1, 600	16.0	1.00*	15.7	1.5	16.8	0.6	------	------	18.7	1.00*	------	------	19.8	0.01*	19.0	0.5*	18.4	0.02*
	1, 550	12.8	0.01*	16.3	0.01*	18.4	.00	------	------	19.0	0.00	------	------	19.4	.01*	19.4	.01*	20.6	.02
	1, 500	15.4	.01*	17.4	.01	18.7	.01	------	------	20.0	.00	------	------	20.3	.00*	20.0	.00	20.0	.00
	1, 450	15.6	.02	17.3	.03	18.9	.06	------	------	19.4	.00	------	------	20.0	.02*	20.0	.00	21.1	.01
	1, 400	16.5	3.3	15.9	4.5	------	------	------	------	19.5	.01	------	------	20.6	.02*	19.8	.01	20.2	.50
	1, 350	------	------	------	------	------	------	------	------	19.2	.60	------	------	20.5	3.2	19.8	.04	------	------
SrO	1, 650	------	------	17.5	1.7	------	------	------	------	------	------	------	------	------	------	------	------	------	------
	1, 600	------	------	18.9	0.04	------	------	------	------	------	------	------	------	------	------	------	------	------	------
	1, 550	------	------	20.6	.01	------	------	------	------	------	------	------	------	------	------	------	------	------	------
	1, 500	------	------	19.7	1.14	------	------	------	------	------	------	------	------	------	------	------	------	------	------
MgO	1, 650	------	------	20.3	0.01	------	------	------	------	------	------	------	------	------	------	------	------	------	------
	1, 600	------	------	19.4	.02	------	------	------	------	------	------	------	------	------	------	21.0	.32*	------	------
	1, 550	------	------	19.8	.00	------	------	------	------	------	------	------	------	------	------	21.9	.01	------	------
	1, 500	------	------	18.7	.19	------	------	------	------	------	------	------	------	------	------	21.4	.01	------	------
	1, 450	------	------	15.9	5.6	------	------	------	------	------	------	------	------	------	------	19.8	.2	------	------
	1, 400	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	4.3	------	------
SiO_2	1, 700	------	------	18.7	0.00*	16.5	.01*	------	------	18.6	.01	------	------	------	------	18.9	0.00	18.9	.00
	1, 650	------	------	17.4	.00	17.4	.01	------	------	18.4	.02	------	------	17.6	0.00*	19.8	.01	19.8	.38
	1, 600	15.0	0.00*	17.0	.05	15.4	3.9	------	------	17.4	.29	------	------	17.9	.01	17.5	1.8	16.0	6.7
	1, 550	16.7	1.13	14.9	5.9	------	------	------	------	11.6	12.4	------	------	14.3	7.8	14.7	9.1	------	------
TiO_2	1, 650	18.8	0.27*	18.2	0.01*	18.6	0.01*	------	------	21.6	0.01*	20.8	0.01*	------	------	21.3	0.01*	20.8	0.01*
	1, 600	19.2	.62	18.9	.04	20.0	.06	20.3	0.00	21.3	.00	20.8	.01	20.6	0.03	21.1	.00	20.6	.00
	1, 550	18.6	.97	19.8	.08	19.3	.54	20.6	.02	20.8	.06	20.6	.58	20.8	.01	20.6	.00	20.3	.60
	1, 500	19.2	1.19	18.7	1.22	18.7	1.22	20.3	1.82	19.8	2.14	19.8	2.48	20.3	1.10	20.3	1.42	19.8	2.27

		Base composition (mole)																	
		$48BeO:4Al_2O_3:ThO_2$ [c]						$48BeO:Al_2O_3:ZrO_2$ [d]				$24BeO:Al_2O_3:2ZrO_2$ [d]				$24BeO:2Al_2O_3:ZrO_2$ [d]			
		Percentage by weight of oxide added to base composition																	
		8		4		2		4		2		4		2		4		2	
		Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.	Shr.	Abs.
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
CaO	1,650	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	19.0	0.06*	18.1	0.02*	17.9	0.02*	16.8	0.00*
	1,600	-----	-----	16.5	1.9*	17.4	0.8	19.4	0.01	20.3	0.01	19.0	1.0	19.0	.04	18.4	1.1	18.1	.5
	1,550	12.6	4.0*	16.2	0.01*	18.2	.01	19.7	.01	20.8	.02	18.7	0.5	19.4	.07	18.1	1.3	18.7	.2
	1,500	16.7	0.02	18.1	.01	18.2	.01	19.8	.00	19.8	.03	18.7	.6	18.1	1.5	17.8	1.3	18.1	1.2
	1,450	16.2	.04	17.9	.06	18.2	.04	20.6	.02	20.6	.64	-----	-----	-----	-----	-----	-----	-----	-----
	1,400	16.5	4.3	14.9	5.3	-----	-----	19.4	.35	19.0	3.13	-----	-----	-----	-----	-----	-----	-----	-----
SrO	1,650	-----	-----	-----	-----	-----	-----	19.8	.08*	20.0	0.02*	17.9	1.7	18.7	1.0	19.4	0.2*	18.4	0.2*
	1,600	-----	-----	-----	-----	-----	-----	21.5	.6	21.5	.01	19.8	1.3	19.8	0.9	19.5	.9	19.5	.6
	1,550	-----	-----	-----	-----	-----	-----	21.6	.6	21.1	.04	20.0	0.9	20.0	.8	19.7	.5	19.2	.6
	1,500	-----	-----	-----	-----	-----	-----	-----	-----	22.2	.03	-----	-----	-----	-----	-----	-----	-----	-----
	1,450	-----	-----	-----	-----	-----	-----	-----	-----	17.6	.62	-----	-----	-----	-----	-----	-----	-----	-----
BaO	1,700	-----	-----	-----	-----	-----	-----	18.9	3.6*	20.0	.3*	17.9	3.4*	17.3	2.2*	18.2	1.5*	17.6	1.3*
	1,650	-----	-----	-----	-----	-----	-----	20.0	0.4	20.6	.1	19.0	1.3	19.0	1.2	18.9	0.9	18.4	0.8
	1,600	-----	-----	-----	-----	-----	-----	20.0	.4	20.8	.2	19.2	1.2	19.2	1.2	18.1	.8	18.7	.9
MgO	1,700	-----	-----	-----	-----	-----	-----	19.8	.6*	19.2	2.4*	17.4	3.0*	16.0	2.9*	16.0	3.5*	16.8	1.1*
	1,650	-----	-----	-----	-----	-----	-----	20.0	.00	19.5	0.2	18.9	0.8	18.9	0.9	17.6	1.0	18.2	0.7
	1,600	-----	-----	-----	-----	-----	-----	20.0	.01	20.0	.9	18.0	1.1	18.0	1.5	17.0	2.1	17.5	1.5
	1,550	-----	-----	-----	-----	-----	-----	21.3	.01	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
	1,500	-----	-----	-----	-----	-----	-----	20.6	.00	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
	1,450	-----	-----	-----	-----	-----	-----	19.8	.01	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
	1,400	-----	-----	-----	-----	-----	-----	17.3	3.93	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
SiO_2	1,700	-----	-----	17.9	0.00*	16.8	.00*	18.5	0.9*	18.7	.6*	18.1	1.6*	16.8	1.3*	17.9	1.3*	16.8	1.0*
	1,650	-----	-----	17.4	.00	17.1	.01	18.1	1.3	18.2	1.6	17.3	1.9	17.3	1.9	16.5	1.3	17.3	1.4
	1,600	15.2	0.00*	17.0	.06	16.5	2.8	17.1	3.1	14.9	7.0	16.8	2.5	15.5	4.2	16.3	2.1	16.0	3.6
	1,550	15.5	.05	14.4	6.4	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
	1,500	15.6	2.6	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
TiO_2	1,700	-----	-----	-----	-----	-----	-----	20.6	0.8*	20.0	0.4*	19.0	1.0*	17.6	0.9*	18.7	2.2*	17.4	1.0*
	1,650	-----	-----	19.2	0.02*	18.4	0.01*	20.0	.7*	20.0	.3*	18.1	1.0	18.4	.9	19.0	0.9	19.4	0.7
	1,600	18.9	0.03	18.6	.01	19.0	.00	21.1	.3	21.5	.04	19.8	1.1	20.1	1.4	19.8	1.0	20.0	.9
	1,550	18.5	.07	19.2	.10	19.2	.31	20.0	2.4	19.4	3.3	18.1	2.4	16.0	4.8	19.0	1.7	16.5	4.1
	1,500	18.9	.90	19.0	.85	18.4	1.52	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

[a] Vitrified specimens of the base composition without oxide additions were obtained by heating at 1,650°, 1,700° C, and 1,750° C.

[b] Vitrified specimens of the base composition without oxide additions were obtained by heating at 1,600°, 1,650°, 1,700°, 1,750°, and 1,800° C.

[c] Vitrified specimens of the base composition without oxide additions were obtained by heating at 1,700° and 1,750° C.

[d] Vitrified specimens of the base composition without oxide additions were not obtained.

cal and electrical properties; and, second, as both the raw materials and production processes under plant conditions are apt to introduce extraneous oxides, it should be helpful if the manufacturer could estimate in advance what to expect from such additions. Accordingly, 2-, 4-, and 8-percent additions of PbO, CaO, SrO, BaO, MgO, B_2O_3, SiO_2, and TiO_2 were made to several bodies of the MgO-BeO-Al_2O_3, the BeO-Al_2O_3-ThO_2, and the BeO-Al_2O_3-ZrO_2 series. Values for linear shrinkage and for absorption are summarized in table 15 for those results believed to be of interest.

PbO was added only to compositions of the MgO-BeO-Al_2O_3 series. No values are presented for this series because there appeared to be little promise of improvement by means of the oxide additions, which included B_2O_3 and TiO_2 in addition to PbO.

(a) BeO-Al_2O_3-ThO_2 SERIES

Five compositions and additions of five oxides were investigated in this series, although each of the five oxides was not added to each of the base compositions. Additions of 4 percent of CaO, of MgO, or of SiO_2 to the mole composition BeO:Al_2O_3:2ThO_2 produced no useful specimens, and the data are therefore not presented. The summary of results for the other four compositions (table 15) shows that some of the additions effected an appreciable lowering of the vitrification range, and the addition of 2 or 4 percent of CaO also widened this range for the 96:1:1 and 48:4:1 compositions. In general, 4-percent additions were the most beneficial. Specimens containing CaO were grayish in color, and a tendency to produce a low viscosity glass that segregated in the lower portions of a specimen increased wish increase in CaO. For example, no satisfactory test pieces were obtained with the 160:2:1 composition containing 8 percent of CaO, but a 2-percent addition of CaO to this base composition, and heating at 1,500°, produced bodies of good texture and with an average strength in compression of 188,000 lb/in^2. The same base composition with no additions, and heated at 1,725° C., had an average strength of 244,000 lb/in^2. With a 4-percent addition of MgO, vitrification was obtained at 1,500° and 1,550° C. Four-percent additions of SrO or MgO to the composition 24BeO:Al_2O_3:ThO_2 produced good specimens at 1,550° and 1,600° C.

Additions of SiO_2, with the possible exception of 4-percent additions to the 48:4:1 and 24:1:1 compositions, were not beneficial. The color of specimens containing TiO_2 was generally some shade of buff. The 8-percent addition to 24BeO:Al_2O_3:ThO_2 was definitely harmful, but 8 percent added to the other three bodies, and 2- or 4-percent additions to all of the four bodies (table 15) lowered the minimum vitrifying temperature to 1,550° C., and the range is from 1,550° to 1,600° C. Three specimens of 160BeO:2Al_2O_3:ThO_2 with an addition of 2 percent of TiO_2, and heated at 1,550°, had an average strength in compression of 250,000 lb/in^2.

Electrical resistivity and relative thermal conductivity values for specimens of composition 24BeO:Al_2O_3:ThO_2 are given in table 16. The values indicate an appreciable increase in electrical resistance by 4-percent additions of CaO, SrO, or MgO and a decrease by additions of SiO_2 and TiO_2. The 4-percent addition of MgO increased the thermal conductivity slightly, and the other oxide additions lowered it about 50 percent.

(b) BeO-Al_2O_3-ZrO_2 SERIES

As stated previously, only one of the compositions investigated in this system ($48BeO:Al_2O_3:ZrO_2$) even approached vitrification when no auxiliary fluxes were used. It is evident from the values in table 15 that oxide additions to three compositions resulted in some improvement. Two percent of CaO in $24BeO:Al_2O_3:2ZrO_2$ produced vitreous specimens at 1,550° and 1,600° C. Both 2- and 4-percent of CaO, and 2 percent of SrO, in composition $48BeO:Al_2O_3:ZrO_2$ produced satisfactory vitrification ranges. In this same composition, 2 percent of TiO_2 was helpful, but the effect of 4 percent of MgO was the most pronounced in lowering and lengthening the vitrification range. The color of all the specimens was some shade of buff or ivory.

It was noticeable, in handling the vitreous specimens of this system, that they are much more resistant to chipping, and to mechanical shock generally, than is true of the bodies containing ThO_2. Their resistance to crushing also is good as shown by the following values:

$24BeO:Al_2O_3:2ZrO_2$ +2% CaO (matured at 1,575° C.)__________249,000 lb/in².
$48BeO:Al_2O_3:ZrO_2$ +2% CaO (matured at 1,550° C.)__________251,000 lb/in².
$48BeO:Al_2O_3:ZrO_2$ +4% MgO (matured at 1,625° C.)__________275,000 lb/in².

TABLE 16.—*Electrical resistivity (T_e) and relative thermal conductivity values showing effect on these properties of minor oxide additions to compositions in the* BeO–Al_2O_3–ThO_2 *and* BeO–Al_2O_3–ZrO_2 *systems (each value represents 1 specimen)*

Specimen from test No.	Base composition (mole)			Oxide added	Matured at—	Absorption	Electrical resistivity (T_e value)[a]	Thermal conductivity[b]
	BeO	Al_2O_3	ThO_2					
					° C	*%*	*° C*	
233-L	24	1	1	None	1,650	0.01	945	----------
300-L	24	1	1	do	1,750	.02	----------	11
248-L	24	1	1	4% CaO	1,500	.01	1,025	----------
252-L	24	1	1	do	1,550	.01	----------	6
250-L	24	1	1	4% SrO	1,600	.00	1,100	----------
268-L	24	1	1	do	1,550	.01	----------	6
286-L	24	1	1	4% MgO	1,550	.00	1,045	----------
281-L	24	1	1	do	1,600	.02	----------	14
247-L	24	1	1	4% SiO_2	1,650	.00	775	----------
250-L	24	1	1	do	1,600	.05	----------	5
255-L	24	1	1	4% TiO_2	1,650	.01	735	----------
241-L	24	1	1	do	1,600	.04	----------	5
	BeO	Al_2O_3	ZrO_2					
164-L	48	1	1	None	1,750	.42	1,055	10
229-L	48	1	1	4% CaO	1,500	.00	1,065	8
233-L	48	1	1	4% SrO	1,650	.08	990	11
279-L	48	1	1	8% MgO	1,450	.01	----------	33
286-L	48	1	1	do	1,550	.00	858	----------
205-L	48	1	1	2% TiO_2	1,700	.42	755	14

[a] The T_e value for electrical resistivity is the temperature at which, by calculation based on test values, a 1-cm cube of the material has a resistance of 1 megohm. The values were determined by E. N. Bunting.

[b] The thermal-conductivity value is the reciprocal, multiplied by 100, of the temperature drop through a 0.5-in. height of specimen approximately ½ in. in diameter and resting on a hot plate at about 250° C. The values were determined by E. N. Bunting.

An exploratory series of tests, made by substituting MgO, CaO, or SiO_2 for the BeO in $6BeO:Al_2O_3:5ZrO_2$ and $BeO:Al_2O_3:2ZrO_2$, did not produce vitrification. The same comment applies to trials in which 4 percent of the oxides mentioned was added to these compositions. As no data of value were obtained, they are not tabulated.

The values in table 16 indicate that SrO, MgO, and TiO_2 additions to bodies of this series would lower the electrical resistance and that MgO would increase the thermal conductance. Otherwise, the additions had no significant effect.

V. SUMMARY

In order to supply fundamental information upon which to base the practical development of new ceramic compositions for service conditions of increased severity, there was undertaken a study of the characteristics of variously heated oxides in simple binary and ternary combinations. The oxides used in these simple combinations were MgO, CaO, BaO, BeO, Al_2O_3, ThO_2, and ZrO_2. The investigation included the study of phase relations as well as the fabrication and testing of specimens for mechanical and electrical tests, and for other properties having a bearing on their usefulness. The work was supplemented by a limited study of the effects of minor additions of CaO, SrO, BaO, B_2O_3, SiO_2, TiO_2, or PbO. The materials were of the highest purity obtainable commercially. Temperatures ranging from about 1,450° to over 1,900° C. were obtained in an especially designed furnace heated electrically with ThO_2-Y_2O_3 resistors.

In the system BeO-Al_2O_3, large crystals, and also vitrified specimens, of chrysoberyl (BeO.Al_2O_3) were obtained readily. Two eutectics, one at 1,880° C. and 14 wt. percent of BeO, and one at 1,865° C. and 26.9 wt. percent of BeO, were indicated. The electrical resistance of chrysoberyl was very good (T_e=1,285° C.), but the strength in compression and thermal conductivity were only fair. The linear thermal expansion was 0.788 percent between room temperature and 1,000° C. Tests were made also on specimens of BeO and of Al_2O_3 containing small but differing amounts of impurities.

In the system MgO-BeO a simple eutectic was indicated at 1,855° C and 48.2 wt percent of BeO. Compositions containing not less than about 79 wt percent of BeO could be vitrified. Strength in compression was fairly high, electrical resistivity was very good, and the thermal conductivity of bodies containing not more than about 29 wt percent of MgO was practically equal to that of pure BeO.

In the system MgO-Al_2O_3, a limited number of tests were made on the compound $MgAl_2O_4$ (spinel). It was noted that heating at 1,650° was sufficient for an 80- to 90-percent conversion of a MgO-Al_2O_3 mixture to spinel, and specimens heated at 1,900° C were not completely vitreous. The T_e value for spinel was 1,170° C, and the thermal conductivity value was 1.9.

Approximate fields of stability were established for the system MgO-BeO-Al_2O_3, including a small field near the Al_2O_3 apex for what is believed to be a ternary compound. The lowest fusing eutectic, having the composition (by weight) 44.4 percent of MgO, 27.5 percent of BeO, and 28.1 percent of Al_2O_3 (4MgO:4BeO:Al_2O_3, mole ratio), fused at 1,640° C. A considerable range of compositions could be formed into vitreous specimens of which many, particularly those in the high BeO area, had high resistance to crushing, good dielectric properties, and high electrical resistivity, as well as high thermal conductivity. For example, specimens of mole composition MgO:24BeO:Al_2O_3 had an average strength in compression of 286,000 lb/in.^{2}, a dielectric constant (*K* value) of 6.9, and a power-loss factor of 0.06 percent. The T_e value ranged from 1,137 to 1,210, and the average thermal conductivity value was 10.

In the CaO-BeO-Al_2O_3 system, the eutectic in the subordinate system CaO-BeO was found at 1,405° C and approximately 65 wt percent of CaO. In general, the "vitrification surface" is about 100 deg C lower than for the MgO-BeO-Al_2O_3 system, but the test pieces were coarsely crystalline, and none was prepared for test.

The system BaO-BeO was investigated only superficially. No specimens for mechanical or electrical tests were prepared. The thermal reactions may be complicated by a low-temperature eutectic between BaO and $BaCO_3$.

The system BeO-Al_2O_3-ThO_2 is distinctively one of high temperatures. The eutectic in the Al_2O_3-ThO_2 system occurs at 1,910° C and 60.7 wt percent of Al_2O_3, and the lowest fusing ternary eutectic was found at 1,795° C, and probably is near the mole composition 4BeO:$2Al_2O_3$:ThO_2. The optimum temperature interval for producing vitreous specimens lies between 1,600° and 1,750° C. For mole compositions 160BeO:$2Al_2O_3$:ThO_2 and 48BeO:Al_2O_3:ThO_2, average strengths in compression were, respectively, 244,000 and 279,000 lb/in^2. Power-loss values were less than 0.01 percent, and the dielectric constant ranged from 7 to 8.

The BeO-Al_2O_3-ZrO_2 system resembles the BeO-Al_2O_3-ThO_2 system as regards phase relations, but the beginning of fusion of corresponding ternary mixtures will average about 50 deg C lower. Fusion for the Al_2O_3-ZrO_2 eutectic was observed at 1,885° C and the composition, by weight, was 55 percent of ZrO_2 and 45 percent of Al_2O_3. The lowest ternary eutectic is indicated to be at about 1,750° C and the mole composition 2BeO:Al_2O_3:ZrO_2. The nearest approach to vitrification was obtained with the mole composition 48BeO:Al_2O_3:ZrO_2, which had an average absorption of about 0.4 percent when heated at 1,750° C. No specimens were prepared for mechanical or electrical tests.

Tests for determining relative resistance to attack by PbO liquid and vapor indicate (a) that attack by the liquid on immersed test pieces is much greater than by the vapor on pieces supported above the liquid, (b) that attack at 1,100° C is much greater than at 1,000° C, and (c) that siliceous bodies were the least, and "high BeO" bodies the most, resistant to attack.

Additions up to 8 percent of an auxiliary oxide, such as PbO, CaO, SrO, BaO, MgO, B_2O_3, SiO_2, or TiO_2, did not improve significantly the vitrification behavior of compositions in the system MgO-BeO-Al_2O_3. In the system BeO-Al_2O_3-ZrO_2, additions of CaO or MgO were the most effective in producing vitreous specimens, but the composition range was very limited. Auxiliary oxide additions to four compositions in the BeO-Al_2O_3-ThO_2 system effected a lowering of at least 50 deg C in the minimum vitrification temperature in most cases. CaO in 4-percent additions was the most beneficial and, for one composition (160BeO:$2Al_2O_3$:ThO_2), vitreous pieces were obtained at 1,350° C. Specimens of this composition with an addition of 2 percent of TiO_2 had an average strength in compression of 250,000 lb/in.^{2}. Four-percent additions of CaO, SrO, or MgO increased the electrical resistance of the mole composition 24BeO:Al_2O_3:ThO_2, but SiO_2 or TiO_2 additions lowered it. The 4-percent addition of MgO increased the thermal conductivity slightly, but the other oxide additions lowered the conductivity about 50 percent.

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WASHINGTON, October 10, 1945.