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Characterizing ceramic integrated circuit packaging materials

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San Jose State University, 1992

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CHARACTERIZING CERAMIC INTEGRATED CIRCUIT PACKAGING MATERIALS

A Thesis

Presented to

The Faculty of the Department of Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

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December, 1992

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ABSTRACT
CHARACTERIZING CERAMIC I.C. PACKAGING MATERIALS
by Mary Beth Lange

The important properties of an integrated circuit packaging material are identified. The theoretical basis for these properties is examined and the processing parameters that affect them are discussed.

Commercial samples of various purities of the popular packaging material alumina, as well as the specialty materials beryllia, silicon carbide, aluminum nitride, and NTK's new glass-ceramic composite FC-01 were tested. The important electrical, thermal, and mechanical properties of each material were measured and compared to the manufacturer's quoted value and to values found in the literature. The discrepancies between these values are explained in terms of the composition, processing, and testing conditions of the packaging material.

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1. REVIEW OF CERAMIC PACKAGES

Ever since the invention of the integrated circuit in 1959, there has been a tremendous demand for smaller, lighter, yet more powerful semiconductor circuits. Often the limiting factor in the size, cost, and performance of the device is not the semiconductor device itself but its package. Packaging technology must keep pace with these smaller and more powerful semiconductors in order to allow higher levels of integration and greater performance in less space without compromising quality and reliability.

There are basically three types of single chip package designs in use: Dual In line Package (DIP), Chip Carrier (CC), and Pin Grid Array (PGA), as shown in Fig 1.[1] The characteristics of these and other packages are summarized in Table 1. The first package to be introduced and the type used for approximately 80 percent of today's devices is the DIP.[2] The DIP has a simple rectangular housing with two rows of metal leads, one along each long edge. The DIP is attached to a printed circuit board by inserting the leads through holes in the board and then soldering them. A primary function of the DIP is to spread the electric signal from the chip input/output pads (0.025 mm apart) to the package leads (0.25 mm apart). The package also provides protection from the environment for the chip, and thermal paths to dissipate heat. However, the DIP cannot meet the needs of complex very large scale integrated devices with a large number of leads.[3] As can be seen in Table 1, the maximum number of leads (or pins) possible for the DIP is only 64. To achieve the maximum number of leads, the DIP will have to be 0.9 inch by 3.2 inches, making it up to 50 times larger than the chips themselves, and thus working against efforts to miniaturize the devices.

1a. DUAL-IN-LINE
(DIP)

1c. CHIP CARRIER

1b. PIN GRID ARRAY
(PGA)

FIGURE 1. Single Chip Package Designs [1].

Table 1. Integrated Circuit Package Characteristics [2]

Type	Maximum Number of Pins	Typical Board Area (square inch)	Relative Material Cost	Relative Thermal Dissipation	Date of Introduction	1985 Annual Worldwide Use (Millions)
DIP	64	1.17	Low	Fair	Mid 1960s	15,665
Chip Carrier	84	0.33	High	Good	Late 1960s	184
Leadless Chip Carrier	124	0.31	High	Good	Late 1970s	82
PGA	256	NA	Very High	Excellent	Mid 1970s	5

In an attempt to decrease the size of the DIP, the Small-Outline Integrated Circuit package (SOIC) was developed. The SOIC is basically a DIP, but it is shorter, flatter, and has 50 mils between leads rather than 100 mils, as in the standard DIP. The main problem, however, is that the SOIC can only accommodate 28 pins.

In the computer industry where many VLSI chips with a large number of leads are used (e.g., in microprocessors) the PGA is popular. Its maximum number of leads is a phenomenal 256. They are densely packed in a 100 by 100 mil grid pattern on the bottom side of the package and are mounted onto the circuit board using the same insertion mounting technique as with the DIP.

The third type of package, the chip carrier (CC), has leads spaced typically 50 mils apart (with a growing trend to 25 mils) on each side of the square package. Besides weighing significantly less than the DIP for the same number of pins, CCs--along with SOIC packages--have the tremendous advantage of Surface Mount Technology (SMT) (A comparison of the weights of CCs versus DIPs, as a function of pins is shown in Fig. 2). In SMT, the packages are soldered directly onto the surface of the circuit board without inserting the leads through holes in the board, as can be seen in Fig. 3. The main advantage of SMT is that it allows

FIGURE 2. The Weight of Various Chip Carriers for SMT Compared to the Weight of an Equivalent DIP [4].

FIGURE 3. Insertion Mounting (A) vs. Surface Mounting (B) [2].

for a large increase in packing density, reducing the board size by an average of 50 percent as shown in Figure 4. Packages can be mounted closer together since holes do not have to be drilled into the board. Also both sides of the board can now be used. Another advantage is that the board has fewer layers and no machining costs, leading to a cost reduction of 30 percent or more through decreased materials and labor costs.[4]

The worldwide usage of the various types of packages is changing quite rapidly, as can be seen in Figure 5. The DIP is expected to drastically decrease in usage for the following reasons: too few pins, too large a size, and inability to be surface mounted. The SOIC is expected to increase in usage since it can be surface mounted. In cases where more pins are required, the CC is expected to dominate.

Plastic packages will be used more readily than ceramic packages because they are less expensive. However, ceramic packages offer many advantages over the plastic packages. The first and most critical of these is better hermetic sealing at the ceramic/metal interface. The problem with a nonhermetic seal is that moisture can enter the package, thus allowing the aluminum metallization to grow dendrites.[1] This phenomenon results in shortcircuiting between metallizations or the depletion of metal to the point that the circuit is open (loss of electrical continuity). The ceramic package also allows a finer pattern capability and therefore allows more integrating or combining of individual circuit elements into one discreet package. The ceramic package dissipates heat better and is less vulnerable to chemical attack during soldering and cleaning operations. Lastly, the ceramic package has better dimensional stability, especially at elevated temperatures. Its coefficient of thermal expansion is less dependent on temperature. It is also less prone to physical distortion, as characterized by warpage and loss of flatness.

Ceramic packages can be one single layer, or to allow more circuitry in less surface area, they can be multi-layered. The fabrication costs make multilayered packages more expensive than single layered ones. The multilayer construction consists of 5 to 25 mils thick layers of ceramic tape, each having metallized circuit patterns.[6] Conductive vias forming electrical interconnections between circuits pierce the tape layers, and holes and cavities are punched out as required. These layers are then laminated under pressure

FIGURE 4. Comparison of Printed Circuit Board (PCB) Level Area with DIP Packaging and SMT Packaging [4].

FIGURE 5. Worldwide IC Package Consumption [5].

and both the metallized layers and ceramic are co-sintered at 1600°C, thus becoming a monolithic structure with a three dimensional wiring system. The major advantages of this multilayer structure include the following: faster switching speeds due to shorter signal paths, greater device density due to more circuit layers, increased thermal conductivity, and hermeticity. A cross-section of a typical multilayer package is shown in Figure 6.

The most common multilayered ceramic package is constructed from alumina, with tungsten or molybdenum conductors. Refractory metals must be used because of the high (1600°C) processing temperature required for the sintering of alumina. Aluminum nitride (AlN) co-fired packages have recently appeared on the market after overcoming a variety of processing problems including AlN's inferior (compared to most oxides) wettability by metals.^[7] Much effort is being devoted to developing a low temperature process which would allow for the usage of copper connections. This would be a tremendous breakthrough as the electrical conductivity of copper is superior to the refractory metals, allowing for a faster, smaller circuit.

FIGURE 6. Cross Section of a Typical Ceramic Multilayer Package [7].

2. OBJECTIVES OF INVESTIGATION

Commercially available packaging materials have a wide range of characteristics, with properties for the same material varying from manufacturer to manufacturer. Independent measurements of properties of commercial ceramic packages are not commonly published in technical or scientific journals.

The objectives of this study, therefore, consist of the following:

- a) Identify those properties which are important for packaging materials.
- b) Provide the theoretical basis for the properties.
- c) Identify processing parameters that affect these properties.
- d) Measure critical thermal, electrical and mechanical properties of commercially available packages, and compare them to literature values.

3. DESIRED PROPERTIES OF A PACKAGING MATERIAL

Because the final device operation depends heavily on the package and thus, the packaging material, the properties of this material are paramount to the chip's performance. The characterization of these materials is often times not a sufficient measure of how the material will behave under actual working conditions. Many manufacturers will simply quote a room temperature value of a given parameter from a reference such as a textbook or handbook. The values of interest are those over the temperature range of operation (many parameters are temperature dependent) as well as the values from that particular manufacturer or, if possible, that particular batch. Each parameter will be a function of that manufacturer's processing conditions and starting materials, both of which affect the final package's chemical composition and microstructure. Because of the lack of quality control of incoming materials (e.g., particle size, impurities) and variance in the processing, there is a high probability for parameters to change not only from manufacturer-to-manufacturer, but from batch-to-batch.

Additionally, while one property may be especially critical, all properties need to be considered. For instance, a product engineer at an electronics company may want to make the fastest device possible and therefore choose a package made from the lowest dielectric constant. This package, however, may also be made using a material with a low thermal conductivity such that the product's reliability will suffer. In other words, all properties should be considered when selecting a package. What follows is an overview of these desired properties.

3.1 Thermal Properties

3.1.1 Thermal Conductivity

One of the most critical properties of a packaging material is that it have a high thermal conductivity. This aids in dissipating the heat generated from running the device and is becoming increasingly important as chips are mounted closer together and the circuits are more dense. Typical operating temperatures of a silicon IC can be 125°C to 175°C and as high as 300°C for more

demanding operations.[9] The mean time to failure of the device increases by 10 percent for each one degree reduction in temperature of the device, making the incentives great to increase the heat dissipation from the chip environment.[10]

Thermal conductivity is the rate of heat flow through a material and is usually reported in units of cal/sec cm °C, where calories represents the amount of heat, and cm is the distance the heat is traveling.[10] The thermal conductivity (k) is directly proportional to the heat capacity (c), the quantity and velocity of the carriers (v), and the mean free path of the carriers (mfp), as represented by Equation (1):[11]

$$k \propto cv(mfp) \quad (1)$$

Thermal conductivity can therefore be increased by increasing the heat capacity, increasing the number of carriers and their velocity, and/or increasing the mean free path (i.e., decreasing scattering) of the carriers.

Most organic materials have low thermal conductivity due to covalent bonding, large molecule sizes, and lack of crystallinity. Ceramics, on the other hand, are capable of much higher thermal conductivities, as can be seen from Figure 7. Ceramics having the greatest thermal conductivity are those with structures composed of a single cation, structures comprised of cations of similar atomic weight, and structures without extraneous cations in solid solution. High thermal conductivities are also found in ceramics such as SiC, which is composed of elements having a low atomic weight, high bonding strength, and having a crystal structure with a diamond, zinc blende, or wurtzite type.[12]

Another factor that affects the thermal conductivity of a ceramic is the amount and type of impurity atoms. Impurity atoms decrease the mean free path thereby decreasing the thermal conductivity. Temperature also has a strong effect because the mean free path is inversely proportional to the temperature. Lastly, radiation of heat can increase thermal conductivity in the case of porous ceramics.[12] The increase in conductivity with temperature observed for powdered magnesia and insulating firebrick, as shown in Fig.7, is due to radiation across the pores.

FIGURE 7. Thermal Conductivity vs. Temperature for Ceramic, Metallic, and Organic Materials [13].

3.1.2 Coefficient of Thermal Expansion

A second thermal property which should be considered is the packaging material's coefficient of thermal expansion (CTE). It is very important that the CTE be as close to that of the silicon chip as possible. A severely mismatched chip and package can result in die-bond failure. This is also a function of the die-bond material used and its ability to withstand stresses. Thermal shock damage, the most common failure mode of IC packages, is also strongly dependent on the CTE. Damage due to thermal shock can lead to subsequent damage by moisture intrusion into the chip environment.^[10]

The effect of thermal shock, which induces stresses in a component as a result of a temperature difference between the surface and interior regions is also related to the CTE.^[13] The peak stress typically occurs at the surface during cooling, and its magnitude is given by the Equation (2).

$$\sigma = E\alpha(T_i - T_f) / 1 - \nu \quad (2)$$

where σ is the thermal stress, E the elastic modulus, α the coefficient of thermal expansion, ν is Poisson's ratio, and $T_i - T_f$ is the difference between the final temperature and the initial temperature.

Equation (2) indicates that to decrease the thermal stress, the elastic modulus and CTE should be as low as possible. The imposed temperature difference should also be minimized. One means of decreasing the temperature difference is to increase the thermal conductivity of the material. Of these factors, the CTE is most critical for semiconductor applications since the package is continually temperature cycling and a large CTE mismatch could impact package reliability.

The CTE is defined as follows:

$$\alpha = l_i - l_f / l_i(T_i - T_f) \quad (3)$$

where l_i is the length at room temperature and $l_i - l_f$ is the change in length

for a given temperature change. As can be seen from Figure 8, the temperature dependence of the CTE parallels that of heat capacity.^[14]

The CTE is also closely related to crystal structure, grain size, and bond strength. Materials with a less dense, open structure, a small grain size, and high bond strength have the lower CTEs, as shown in Figure 9 for a wide variety of materials.

3.2 Electrical and Dielectric Properties

3.2.1 Dielectric Constant

The most critical electrical property of a packaging material is that it have a low dielectric constant since this is the parameter of the ceramic most closely tied to the speed of the device. Although this is the most important property of the ceramic, the speed of the package is also determined by the conductivity and length of the metallic leads. The ceramic must allow the processing of increasing numbers of signals at increasing speeds by electrically isolating the metallic conductors that are printed across and through it. Two signal-carrying leads with a ceramic in between them can be thought of as a capacitor with capacitance as follows:

$$C = kA/d \quad (3)$$

where A is the area between leads, d the distance between leads, and k is the dielectric constant. Thus, if k is large, current can be drained from the signal line and the speed of the circuit is slowed down.

A measure of the amount that the speed of the circuit is slowed down is called the time delay (Td) of the signals, which is given by Equation (4):

$$Td = k^{1/2}l/c \quad (4)$$

where k is the dielectric constant, l the distance the signal travels, and c the speed of light.

Another reason for the use of materials with low dielectric constants is to reduce the electrical noise that is generated when high speed signals

FIGURE 8. Parallel Changes in Heat Capacity and Thermal Expansion Coefficient of Al_2O_3 [14].

FIGURE 9. Thermal Expansion Characteristics of Typical Metals, Polymers, and Ceramics [13].

propagate through the package.^[4] Three important sources of noise-- crosstalk between adjacent signal leads, pulse reflections from impedance discontinuities, and simultaneous switching noise--can all be reduced by using a lower capacitance material or more effectively by using multilayer, multichip packages.

The dielectric constant refers to the total polarizability that occurs resulting from a combination of electronic, ionic, and dipole orientation effects when the material is placed in an electric field. For multiphase materials, the dielectric constant can be determined by using the logarithmic mixture rule given by Equation (5):

$$\log k = \sum_i v_i \log k_i \quad (5)$$

where k is the dielectric constant and v_i is the volume fraction of each phase. The bulk dielectric constant is therefore influenced by the material's chemical purity, porosity, and number and composition of phases.

3.2.2 Dielectric Strength

Another important dielectric property is the dielectric strength, which is defined as the capability of the material to withstand an electric field without breaking down. It has the units of volts per unit of thickness of the dielectric.

$$(V_i - V_f)/(X_i - X_f) = P/\epsilon_0 (1/k - 1) \quad (6)$$

where $(V_i - V_f)/(X_i - X_f)$ is the dielectric strength or $(V_i - V_f)$ is the electric potential difference across a dielectric thickness $(X_i - X_f)$, P the polarization, and ϵ_0 the permittivity of free space.

Typically, single-crystal ceramics have a higher dielectric strength than polycrystalline ceramics. Organic materials also have a high dielectric strength which is one of the reasons why they are widely used as electrical insulation.

3.2.3 Dielectric Loss Factor

The last dielectric property to be considered is the dielectric loss factor. This energy loss, $\tan\delta$, is directly proportional to the power dissipation in an insulator or capacitor.^[14] This loss is due to current leakage and dipole friction resulting in energy lost per second as given by equation (7):

$$\tan\delta = \sigma / 2\pi f k' \epsilon_0 \quad (7)$$

where σ is the conductivity, f the frequency, k the dielectric constant, and ϵ_0 the permittivity of free space. The dielectric loss factor of ceramics is small compared to that of plastics and the dielectric losses of single crystals are minimal and are mainly determined by minor impurities.

3.2.4 Electrical Resistivity

Another electrical property to be considered is the material's resistivity. The material must be an insulator in order to electrically isolate the signals and prevent current losses. The electrical conductivity (inverse of resistivity) is somewhat analogous to thermal conductivity where the amount of conduction is a function of the energy present (i.e., size of electric field), the number of carriers, and the amount of dissipation. Insulating ceramics (i.e., those with band gaps greater than 3 eV) have resistivities greater than $10^{14} \Omega\text{-cm}$. The electrical resistivity of some metals, polymers and ceramics is compared in Table 2.

Factors that affect resistivity include composition, impurity/solute concentration, heat treatment, stoichiometry, porosity, point and line defect concentration, and phase distribution. The grain size could also have an effect.

3.3 Mechanical Properties

Mechanical properties, particularly flexural strength and toughness, play a large role in the quality and performance of the packaging material. Today's electronic systems operate in widely varying environments and must be able

Table 2. Electrical Resistivity of Some Metals, Polymers, and Ceramics at Room Temperature [13]

Material	Resistivity ($\Omega\text{-cm}$)
Metallic conduction	
Copper	1.7×10^{-6}
Iron	10×10^{-6}
Tungstun	5.5×10^{-6}
ReO ₃	2×10^{-6}
CrO ₂	3×10^{-5}
Semiconductors	
SiC	10
B ₄ C	0.5
Ge	40
Fe ₃ O ₄	10^{-2}
Insulators	
SiO ₂	$>10^{14}$
Steatite porcelain	10^{14}
Fire-clay brick	10^8
Low-voltage porcelain	$10^{12}\text{-}10^{14}$
Al ₂ O ₃	$>10^{14}$
Si ₃ N ₄	$>10^{14}$
MgO	$>10^{14}$
Phenol-formaldehyde	10^{12}
Vulcanized rubber	10^{14}
Teflon	10^{16}
Polystyrene	10^{18}
Nylon	10^{14}

to survive large changes in temperature and humidity. Even before shipping, the components are subjected to mechanical stresses (e.g., robotic handling during assembly). Chemical attack during soldering and various cleaning operations can also generate mechanical stresses.

The theoretical cohesive strength of a material can be defined as the tensile stress required to break atomic bonds and pull the structure apart and is described by Equation (8):^[13]

$$\sigma_{th} = (E\delta/a_0)^{1/2} \quad (8)$$

where σ_{th} is the theoretical cohesive (or tensile) strength, E the elastic modulus, a_0 the interatomic spacing and δ the fracture surface energy. For ceramic materials, the theoretical strength is typically 1/10 to 1/5 of the elastic modulus.

Under the condition of tensile stress, the material is pulled apart. As the load increases so does the interatomic spacing. The greater the bond strength, the greater the stress required to increase the interatomic spacing, and therefore, the higher the value of the elastic modulus. The bond strength or amount of ionic bonding, as related to the difference in electronegativity, can be seen in Fig. 10. ^[15] The fracture strength of typical packaging ceramics, however, is only about 1/100 of the theoretical cohesive strength. This discrepancy between actual and theoretical strength is commonly observed in all brittle materials, and is due to the presence of flaws such as microcracks, pores, and inclusions. Even a small flaw in a ceramic is critical and can lead to substantial stress concentration. Griffith^[16] related the fracture stress to the material properties and the flaw size by the following equation:

$$\sigma_f = A (E\delta/c)^{1/2} \quad (9)$$

where σ_f is the fracture stress, A a constant depending on specimen and flaw geometries, E the elastic modulus, δ the fracture energy, and c the flaw size.

The ease with which a crack is initiated and propagated is measured by the fracture toughness. The higher the fracture toughness, the more stress necessary to lead to fracture. The critical value of stress which leads to

Figure 10. Bonding Characteristic as a Function of Electronegativity Difference[15]

fracture is the critical stress intensity (K_{IC}) and is an intrinsic property of the material.^[14] For a plane stress,

$$K_{IC} = (2\delta E)^{1/2} \quad (10)$$

where δ is the fracture energy and E the elastic modulus. For an applied stress (σ_a) and crack length $2c$,

$$K_{IC} = \sigma_a Y_c^{1/2} \quad (11)$$

where Y is a dimensionless term determined by the crack configuration.

The flexural strength of a material is also a function of its solute concentration, grain size, and porosity. The major deterrent to the increased usage of ceramic products is its brittleness.^[17] Two techniques that have proven helpful in improving the mechanical properties of ceramics are substrate geometry and microstructural phase control. During processing and commercial use, ceramic packages must be able to withstand mechanical impact. The fracture toughness to prevent crack propagation becomes infinite in the case of point loading. However, it is found that if this same impact is distributed over a slightly rounded convex surface, the force required to propagate a crack is increased by several orders of magnitude.^[18] Today, many high volume dry-pressed substrates are produced with controlled edge geometry (i.e. rounded edges) resulting in marked improvements in circuit reliability and a reduction in assembly line losses.

The second approach to increasing the mechanical reliability of ceramics is similar to that developed by glass manufacturers, namely microstructural control of internal stresses. A prime example is that of the zirconia system where this process is termed transformation toughening.^[19]

Garvie^[20] was the first to successfully increase the toughness and strength in a ceramic material by utilizing the shear strain and volume expansion which occur during the phase transformation from the tetragonal to monoclinic structure. Transformation to the less densely packed monoclinic structure results in a 3 to 5 percent volume expansion which causes microcracking around the transformed particle. However, the theory is that

partially stabilized zirconia (up to 15 percent volume) when added to optimally sized (<5 micron) alumina powder will blunt crack propagation through the composite by the absorption of crack energy through the phase transformation to a more stable structure.

A less effective approach to improving the mechanical properties of ceramics is to reduce the internal stresses by controlling the second phase crystallization. In the common calcia/ magnesia/ silica/ alumina system, the most dense phase is the primary alumina phase (corundum). During heat treatment, any crystallization will generate secondary phases of lower density and higher volume, which in turn will produce internal stresses. Glass, on the other hand, being a highly viscous, low density liquid, will deform and flow when microstresses are applied. Therefore, glass is the only desired second phase in high alumina substrates.

3.4 Other Desired Properties

The two final properties worth considering when choosing a packaging material are weight and cost. Weight is probably the least important of the mentioned properties, but cost is often a determining factor in the decision of which type of packaging material to use. Usually the type of package and packaging material with the best properties (e.g., a multilayer PGA made of AlN or a glass-ceramic) is also the most expensive and increases the cost of the device and therefore, the price of the final product.

4. CERAMIC MATERIALS USED IN ELECTRONIC PACKAGING

4.1 Alumina (Al_2O_3)

Alumina is by far the most widely used ceramic packaging material and was the only ceramic packaging material used during the 1960's and 1970's. Its properties compared to other packaging materials is listed in Table 3. Although alumina is comparable to the other materials in terms of the desired properties of a packaging material, it is greatly inferior in terms of thermal conductivity. However, despite its shortcomings, alumina is most widely used because it is inexpensive, non-toxic, and the "traditional" packaging material, as well as one of the "traditional" ceramic materials.

Table 3. Properties of Packaging Materials

	Al_2O_3	SiC	AlN	BeO
BULK DENSITY (g/cc)	3.6-3.9	>3.1	3.2-3.3	2.9
THERMAL EXPANSION COEFFICIENT ($\times 10^{-6}/^\circ\text{C}$)	6.0-7.0	3.5	4.2-5.7	7.2-8.0
THERMAL CONDUCTIVITY (W/cm $^\circ\text{C}$, @RT)	0.2-0.4	2.7	0.6-1.4	2.0-2.4
DIELECTRIC CONSTANT (MHz)	8.5-10.0	40.0	8.5-10.0	6.5-7.0
BENDING STRENGTH (kg/mm 2)	30-40	40-45	40-50	20

Today, Bayer-processed alumina remains the only raw material available in bulk tonnages, at pennies per pound, with consistently known chemical and physical properties.^[17] All other potential ceramic materials face similar market problems--low volumes, high per pound costs, and a high probability of material variations.

Alumina is manufactured with various degrees of purity. The higher purity alumina (96-99.5%) is used for thick and thin film applications because of its better insulating properties and smooth surface. The percentage of alumina affects the color of the substrate (high purity is white, low purity is dark brown). When high light-shading properties are necessary, 90% alumina can also be used for thick film substrates, providing that the remaining 10% contains materials that make its insulating properties comparable to 96% alumina. The 91 and 92% alumina are used to make ceramic DIPS; it is the least expensive and has the worst insulating properties.

4.2 Beryllia (BeO)

BeO is the second most widely used packaging material and is particularly attractive because of its superior thermal conductivity, which is 8 to 10 times that of alumina. It insulates like a ceramic, but conducts heat almost like a metal. This superior conductivity, however, only exists at room temperature and drops dramatically at higher temperatures (see Fig.11). The thermal conductivity can also vary considerably depending on the porosity and impurity concentration.^[21] As the purity drops below 99.5 percent, the thermal conductivity decreases rapidly.

BeO costs many dollars per pound, is produced only for ceramic application, and thus only in small volumes. As a result of this limited manufacturing experience, its physical properties are more variable. The typical chemistry of Brush-Wellman BeO is shown in Table 4. Silicon and magnesium compounds are added to BeO powder as sintering aids. These impurities are present as a silicate that tends to concentrate in the grain boundaries. BeO does have one major drawback--it is highly toxic. The finished package is entirely safe to handle, but it is the BeO dust occurring

FIGURE 11. Thermal Conductivity of Various AlN vs. BeO and Al₂O₃ [21].

Table 4. Typical Concentration of Impurities in Brush-Wellman BeO [21]

Impurity	Concentration (ppm)		
	Low	Average	High
Al	10	46	82
Fe	17	32	47
Cr	5	8	11
Mn		<2	
Ni	6	9	12
B		2	
Ca	8	31	54
Co		<1	
Cu		3	
Si	1601	1861	2121
Mg	780	922	1064
Li		2	
Zn		<20	
Ti	1	5	9
Cd		N.D.	
Na	119	173	227
Ag		<1	
Mo		<3	
Pb		2	

during manufacturing that is harmful. It is so dangerous, in fact, that BeO is illegal in Japan. It is legal in the U.S.A.

4.3 Silicon Carbide (SiC)

SiC is the least used of the ceramic packaging materials. It is 20 to 100 times more expensive than alumina and has a dielectric constant 4 to 5 times that of alumina. It does, however, have remarkable thermal properties compared to the other ceramics. When SiC is hot pressed with 2 weight percent of BeO, its thermal conductivity is slightly higher than BeO itself.^[22] Its thermal expansion coefficient is almost a perfect match with silicon ($CTE_{SiC} = 3.7 \times 10^{-6}/^{\circ}C$, $CTE_{Si} = 3.5-4.0 \times 10^{-6}/^{\circ}C$). It also has a good flexural strength and toughness.

4.4 Aluminum Nitride (AlN)

AlN has appeared only recently in the marketplace and is presently in the process development phase in many package manufacturer's laboratories. It is expected to overtake alumina as the most widely used ceramic packaging material.^[23] AlN is superior to alumina in all desired properties. Its thermal conductivity is about four times higher than 96 percent alumina, and it is less likely to crack since its bending strength is about twice as high. The AlN substrate also has a thermal expansion coefficient more closely matched to silicon than does alumina.

Although AlN is superior to alumina, its thermal conductivity is still only about 30 percent of BeO and SiC. While the best thermal conductivity of AlN is 200 W/m²C, theoretically it can be 320 W/m²C. Work is being done to attain this theoretical value. One obstacle in achieving this value is that the AlN is difficult to sinter because of its strong covalent bonds. To promote densification, sintering aids must be used. The most successful has been found to be 0.5 to 1.5 weight percent Y₂O₃.

4.5 Composite Materials

The packaging materials of the future are composites.^[7] Designed to take advantage of specific properties of various materials, a composite package can be made by combining AlN with a glass-ceramic such as cordierite or mullite. The AlN contributes a high thermal conductivity while the glass-ceramic contributes a low dielectric constant. The resulting package allows for high speed signal paths as well as the power capability necessary for today's ICs. Such packages can also be made using AlN and a low dielectric constant organic material such as polyimide or polytetrafluoroethylene (PTFE).

5. PROCESSING OF CERAMIC PACKAGING MATERIALS

Two ceramic packages may be made from identical ceramic materials, but it does not necessarily follow that their properties will be the same. The reason for the discrepancy lies in their processing. The first problem area is the difficulty of characterizing the incoming ceramic powder and predicting its suitability for use. The characterization should include the following parameters: particle size, shape, packing, and orientation.^[24] If all these attributes could be quantified, the consistent predictability of raw material to final substrate properties could be feasible. However, problems surround the adequate measurement of several of these variables.

The particle size of the ceramic powder can be readily measured with reasonable accuracy. The problem lies, however, with interpreting the size distribution data. While significant differences in average particle size will differentiate between aluminas of different reactivities, lot to lot variations within the same alumina type have not been detected by particle size analyses. One technique which sums over the entire particle size distribution is surface area measurement. However, slight changes in phase composition may significantly alter the data.

It is possible to measure particle shape, orientation, and packing, but it is very time consuming. In actual practice, these variables are combined with particle size and estimated by measuring the green bulk density. All ceramic fabricators use this one test as the basic control parameter. Providing that the composition is constant, the green bulk density should provide an accurate prediction of the fired dimensions (i.e., shrinkage). However, the problem lies in informing the material supplier of differences in green bulk density since it is actually the summation of four independent variables.

In addition to difficulty in characterizing the starting ceramic powder, substrate variations are also due to uncontrolled oxide-binder interactions. A typical dry press mill formulation is comprised of many raw materials: A binder, B binder, plasticizer, wetting agent, deflocculant agent, antifoam, dye colorant, bacteria control, lubricant, and a release agent. The final properties of the fired substrate are largely determined by these materials and their unfired processing conditions.

A substrate's properties further depend on the forming process used--dry pressed or tape formed. The advantages of each process are listed in Table 5.

Table 5. Comparison of Dry Pressed and Tape Formed Substrates.

Dry Press Substrates			Tape Formed Substrates		
Size control	↑	s	w	↓	Surface defects
Edge configuration		t	e		Board size
Thickness		r	a		Thinness
Multi-holes		e	k		Multi-holes
Hole shapes		n	n		Size control
Thinness		g	e		Thickness
Board size		t	s		Edge configuration
Surface defects		h	s		Hole shapes

Multilayer ceramic packages are tape formed.^[24] Their processing involves many technologies in addition to forming, such as sintering, screen printing, metallization, plating, brazing, and thin film processing. The process steps are shown in Figure 12.

As mentioned previously, the multilayer processing includes cofiring of both the metal and ceramic simultaneously. Because this cofiring is performed at temperatures in excess of 1550°C, the manufacturer is limited to refractory metals. A low temperature process used in the fabrication of cordierite ($2\text{MgO} / 2\text{Al}_2\text{O}_3 / 5\text{SiO}_2$) allows for the use of highly conductive copper.^[25]

Organometallic precursors offer an attractive synthetic route to the formation of amorphous powders which densify at low temperatures by viscous flow. A dense glassy material with the cordierite concentration can be obtained at 850°C prior to crystallization.

Ceramic processing technology is pushed to develop a package for the next generation of very high speed GaAs digital ICs where signal traces must be deposited over materials with dielectric constants less than 3.0.^[26] One approach being tested is sol gel processing of SiO_2 which is described in Figure 13. This process yields a dielectric constant of 2.2.

FIGURE 12. Multilayer Ceramic Package Process.

FIGURE 13. Flow Chart of Processing of Sol-gel Derived Silica Films.

6. EXPERIMENTAL PROCEDURE

Commercially available Al_2O_3 , BeO, AlN, SiC, and FC-01 substrates for packaging were obtained from several manufacturers. The substrate material, manufacturer, and the tests performed to evaluate the properties of each of the samples are summarized in Table 6. Electrical capacitance (C) was measured using a capacitance meter, specific heat (C_p) was measured using a differential scanning calorimeter, elastic modulus (E) was measured using dynamic mechanical analysis, the apparent density (d) was calculated by measuring the sample dimensions and dividing by its weight, and compositional analysis was done using surface analysis techniques, namely Electron Spectroscopy for Chemical Analysis (ESCA), Auger Electron Spectroscopy (AES), and Energy Dispersive Spectroscopy (EDS). The detailed procedure used to conduct each of these measurements is described in the following sections. Descriptions and photographs of the equipment used are contained in Appendix A.

TABLE 6. Commercially Available Packaging Materials, Manufacturers, and Tests Performed in this Investigation.

MATERIAL	MANUFACTURER	PROPERTY/COMPOSITIONAL ANALYSIS						
		C	C _p	E	d	ESCA	XPS	AES EDX
99.5% Al ₂ O ₃	Coors					X		
	NTK	X		X	X			
	Kyocera							
96% Al ₂ O ₃	Coors					X		X
	NTK	X		X		X		X
	Kyocera				X	X		X
94% Al ₂ O ₃	Coors						X	X
90% Al ₂ O ₃	NTK		X	X		X		
	Kyocera							
AlN	Keramont	X	X	X	X	X		X
	Norton	X	X	X	X	X		X
	Heraeus	X	X	X	X	X		X
	NTK	X				X	X	X
BeO	Brush-Wellman	X	X	X	X	X	X	X
FC-01(glass-ceramic)	NTK	X	X	X	X	X	X	X
SiC	Standard Oil		X	X	X			

6.1. Electrical Capacitance (C)

Capacitance was measured by placing each of the samples between the probes of an HP 16034 C-D sample holder. Because of the set-up of the fixture, the samples stood vertically and the bottom corner of the sample was between the probes. Area of probe was $6.94 \times 10^{-3} \text{cm}^2$. No sample preparation was necessary. The samples as-received were smooth-sided slabs ranging from 1 to 10 cm square and from 0.05 to 0.15 cm in thickness. These "slabs" were actual packages but they were taken before they were machined and attached with metal leads. The samples were placed directly between the probes. The fixture was connected to a HP 4275A multifrequency LCR meter with a frequency of 1 MHz, a signal level of 20 mVrms, and no DC bias. Fifteen measurements of capacitance were taken in different areas of each sample. The capacitance edge effects were considered to be negligible.

6.2. Specific Heat (Cp)

The specific heat of each sample was measured using a DuPont 910 Differential Scanning Calorimeter (DSC). Each cell consisted of a silver heating block into which two low thermal mass aluminum pans of 0.05 ml capacity were placed. One pan contained the sample, which was cut into 0.75 cm disks and weighed on a Mettler balance; the other pan was empty. Thermocouples placed directly on the sample and the reference pans monitored the temperature of each as the heating block was heated from room temperature to 450°C at 6°C per minute. The DSC was connected to an Omnitherm computer which controlled the temperature ramp and measured the heat capacity of the sample. Because several hours were required to collect data, only one run per sample was done. To estimate the run-to-run variation, one sample was measured four times.

6.3. Elastic Modulus (E)

The elastic modulus was measured using a DuPont 981 Dynamic Mechanical Analysis System (DMA). The samples were sawn so that they were 2.0 cm x 1.0 cm with a thickness of 0.05 to 0.15 cm. They were then clamped between the two parallel arms of the DMA. An electromagnetic motor oscillated one arm and the sample at an amplitude of 0.2 mm while a linear variable differential

differential transformer (LVDT) measured both displacement and frequency. As the arms oscillated, the sample was strained. These measurements were performed over a temperature range of approximately -100°C to 150°C at a heating rate of 5°C per minute. The DMA was connected to a HP 9000 computer which controlled the temperature ramp and tracked the elastic modulus at each temperature.

6.4. Apparent Density

The apparent density was measured by weighing each sample on a digital scale and then measuring its thickness, width, and length with a micrometer. The apparent density was then calculated by dividing the weight by the volume.

6.5. Compositional Analysis

Compositional analysis was done by Surface Science Labs in Mountain View, CA. Electron Spectroscopy for Chemical Analysis (ESCA) and Auger Electron Spectroscopy (AES) techniques were used for compositional analysis of the packages. The ESCA was an SSX-100 small spot spectrometer using a monochromatized Al K-alpha source. The major and minor axes diameters were 250 and 150 microns, respectively. For most elements, the limits of detection were between 0.5 and 1.0 atomic percent, while for Be and B the limits were 3 to 5 atomic percent.

The AES analysis was done using a Perkin Elmer S90 scanning Auger spectrometer with a beam diameter between 2 and 3 microns and a limit of detection of 1.0 atomic percent.

A CAMSCAN series 4 SEM was used for both Energy Dispersive Spectroscopy (EDS) as well as obtaining information about the surface morphology. EDS can detect elements with atomic masses greater than sodium that are present in concentrations greater than one weight percent.

7. RESULTS AND DISCUSSION

7.1 Thermal Properties

7.1.1 Heat Capacity/Thermal Conductivity

One of the more critical thermal properties of a packaging material is its thermal conductivity. However, because of the problem with locating the proper equipment to measure thermal conductivity, heat capacity was measured instead. These two properties are directly related, as was described in Section 3.1.1. The bulk thermal conductivity, however, is not only a function of heat capacity but also of purity, porosity, and temperature. Measured values of the specific heat are reported, and compared to manufacturer's values, in Table 7.

TABLE 7. Specific Heats as Measured Compared to Manufacturer's Quoted Values

Material	Specific Heat(cal/g°C)	
	Experimental	Quoted
AlN	0.26 (Hereaus)	N/A
	0.13 (Keramont)	N/A
	0.13 (Norton)	N/A
		N/A
SiC	0.074	N/A
	0.074	N/A
	0.078	N/A
	0.083	N/A
90% Al ₂ O ₃	0.17 (NTK)	0.22(Coors) 0.20 (Kyocera)
92%	0.21	0.19
96%	0.21	0.19
99.5%	0.21	0.19
FC-01	3.21	N/A
BeO	1.94	N/A

Manufacturer's values of heat capacity were obtainable only for Coors and Kyocera aluminas. They quote specific heat values, for 90 percent alumina at

100°C, of 0.22 and 0.20 cal/g°C, respectively. The measured value for 90 percent alumina from NTK was 0.17 cal/g°C (at 100°C). While there is no direct way to know if this value is correct, it is plausible when compared to the other quoted values, and the CRC Handbook of Materials Science quoted value of 0.18 cal/g°C (at 25°C). The difference between the measured value and the quoted values could be due to varying densities of the final product, differing compositions, or different testing techniques.

To investigate the run-to-run variations, the SiC sample alone was tested four times. The measured values are also shown in Table 7 and a maximum 11 percent variation was found in the measurements.

The quoted values of thermal conductivity vary considerably as was shown in Table 3. This was also true for heat capacity. According to Iwase [8], the relative heat capacities rank as follows: $C_p(\text{BeO}) > C_p(\text{AlN}) > C_p(\text{SiC}) > C_p(\text{alumina}) > C_p(\text{FC-01})$. However, the relative values from the experimental results of this study indicate the following relative ranking: $C_p(\text{FC-01}) > C_p(\text{BeO}) > C_p(\text{AlN}) > C_p(\text{alumina}) > C_p(\text{SiC})$. It should be noted, however, that the results for FC-01 and SiC are not very reliable, because the tested piece was very small (only about 20 mg) and the sample may not have been representative of the bulk. If these results are removed from the data, the relative rankings are the same as those of Iwase.

It is obvious that BeO should have the best thermal conductivity because beryllium is a considerably smaller, lighter atom than the other constituents and also has a high bond strength. This allows for a larger mean free path within the material. As described earlier, the thermal conductivity for BeO is greatly dependent on temperature. As the temperature increases, a linear decrease in the phonon mean free path is observed until at high temperatures (~1600°K) when the mean free path is approximately equal to the lattice spacing.[14]

The thermal conductivity of AlN shows large variations. Its thermal conductivity has quoted values ranging from 60 to 200 W/m°C, with a theoretical value of 320 W/m°C. This again is due to processing problems. Since AlN is so difficult to densify, the density will vary tremendously, with a great effect on many of its final properties.

The thermal conductivity for alumina ranges from 18 W/m°C for 90% Al₂O₃, to 21 W/m°C for 96%, and 36 W/m°C for 99.5%. This again is due to the increased amount of glassy phase in the lower purity alumina. The amorphous structure has a smaller mean free path as well as a lower bond strength than does the crystalline structure. It would stand to reason that the FC-01, the glass-ceramic, would have, by far, the lowest thermal conductivity, which it does according to the quoted values.

7.1.2 Coefficient of Thermal Expansion

The coefficient of thermal expansion (CTE) would have been an interesting property to measure because there is a wide range of values quoted for each, as was shown in Table 3. However, the proper equipment to measure this parameter was not available. The relative values of the CTE as quoted by the manufacturers involved in this study are as follows: CTE(FC-01) < CTE(SiC) < CTE(AIN) < CTE(alumina) < CTE(BeO). The goal here is to have a CTE as closely matched to silicon as possible. SiC is a perfect match since it has a CTE identical to that of silicon ($3.8 \times 10^{-6}/^{\circ}\text{C}$). The CTE is most strongly a function of bond strength--the greater the bond strength, the lower the CTE. In conjunction with Figure 10, it can be seen that the relative values of the CTE is directly proportional to the percent of ionic bonding.

The CTE varies with manufacturer primarily due to processing conditions which yield different porosities. The greater the porosity, and thus the lower the density, the lower the CTE. One contribution to the low CTE of FC-01 is that it is considerably less dense than the other materials. For all alumina manufacturers, higher purity alumina results in a higher CTE. The higher purity material is also more dense.

When comparing CTE values, the temperature range over which the CTE is evaluated should also be considered. Often this information is not supplied by the manufacturers, but it has a large effect on the CTE. If the thermal expansion is not linear over all temperature ranges, a different CTE value could apply for different temperatures at which a packaging material is used.

7.1.3 Thermal Shock Resistance

Values for the thermal shock point or the critical temperature required for crack instability are rarely given, but the material's thermal shock resistance can be estimated from its elastic modulus, thermal conductivity, and CTE. As was explained in Section 3.1.2, for increased resistance to crack nucleation with a sudden temperature change, a material should possess a low elastic modulus, a high thermal conductivity, and a low CTE. The CTE is most critical for semiconductor applications.

Comparing these values, none of the materials stand out as being significantly better than the rest. The FC-01, while having the best CTE, has the worst thermal conductivity. The opposite is true of BeO. It has one of the best thermal conductivities, but has the worst CTE. SiC is probably one of the better materials with its superior thermal conductivity and CTE, but it has the highest elastic modulus. AlN is moderate with respect to all parameters. Alumina is probably one of the poorer materials with its relatively high CTE and poor thermal conductivity. As for which purity of alumina has the best thermal shock resistance, it is the same case as with BeO and FC-01, namely the purity with the better thermal conductivity (99.5 percent) also has the worse CTE.

7.2 Electrical Properties

7.2.1 Dielectric Constant

The results of the measured capacitance and calculated dielectric constant are shown in Table 8. There was a large discrepancy in the calculated values compared to the manufacturer's quoted values. There was also a relatively large standard deviation in the capacitance measurements. This is most likely due to the poor contact of the probes to the sample during the measurement. The configuration of the probe station was such that only the very bottom corner of each sample could fit between the probes. This meant that the sample was top heavy, making it difficult to ensure that it was exactly normal to the probe tips. This, combined with the rough surface of the sample, lead to a very poor contact.

Table 8. Experimental Dielectric Constant (k) Compared to the Manufacturer's Quoted Value

Sample	Capacitance(fF)		k Calculated	k Quoted	Difference
	Avg. of 15 measurements				
96% Al ₂ O ₃ (NTK)	43		3.81	9.3	5.49
99.5% Al ₂ O ₃ (NTK)	35		4.40	9.7	5.30
AlN(NTK)	54		3.87	9.0	5.13
AlN(Norton)	32		3.30	8.8	5.50
AlN (Keramont)	17		2.93	N/A	
AlN(Heraeus)	28		3.44	N/A	
FC-01	5		1.07	5.6	4.53
BeO	12		1.59	6.6	5.01

An air gap of 0.04 to 0.24 mm on each side was calculated, as shown in Appendix B1. More accurate measurements could have been obtained had it been possible to make measurements at the center of each sample and to have deposited gold on each side of the sample prior to making the measurement.

The relative calculated values of the dielectric constant are as follows--
 $k(99.5 \text{ percent alumina}) > k(96 \text{ percent alumina}) > k(\text{AlN}) > k(\text{BeO}) > k(\text{FC-01})$.
The impurity type and concentration play the largest role in the varying dielectric constant between the "same" material, but from different manufacturers. Impurities dissolve in the matrix, leading to the formation of a variety of point defects. Dielectric losses, in the case of single crystals, have been found to be determined mainly by minor impurities.^[14]

Judging from the ESCA results in Table 9, the major surface component, regardless of bulk composition, is carbon. Carbon contamination can come from dust, fingerprints, and contamination from plastic bags. Another possibility is from improper burn off of organic binders during sintering.

Table 10 shows the elemental composition after deleting this carbon contamination and re-normalizing the other elements. The three

Table 9 Compositional Analysis of Manufacturer Supplied Ceramic Packages Using ESCA Techniques

Sample	Atomic Percent Units for the Elements Detected												
	Al	Si	Cl	C	Ca	K	Mg	N	O	Na	Cu	Zn	Be
<u>AlN:</u>													
Keramont	5.6	2.4	0.7	63	0.6	0.8	--	4.8	21	0.7	--	--	--
Norton	2.5	2.5	--	75	0.5	--	--	3.0	16	0.3	--	--	--
Hereaus	15.0	--	1.0	46	--	--	--	7.3	30	--	0.8	--	--
NTK	15.0	--	--	48	--	--	--	12.0	24	--	--	--	--
<u>Alumina:</u>													
90‡ NTK	1.6	6.4	--	72	--	--	--	0.6	19	--	--	--	--
96‡ Kyocera	2.9	3.9	--	75	0.2	--	--	0.6	17	--	--	--	--
96‡ Coors	8.4	3.9	--	63	0.4	--	--	1.0	23	--	--	--	--
96‡ NTK	22.0	3.3	--	29	--	--	0.8	1.5	43	0.3	--	--	--
<u>BeO</u>	--	1.2	--	66	--	--	--	1.4	20	0.3	--	--	8.4
<u>FC-01</u>	2.9	12.0	1.2	42	--	--	2.3	3.7	34	0.5	--	0.5	--

Table 10 ESCA Results After Normalizing for Carbon Contamination

Sample	Atomic Percent Units for the Elements Detected										
	Al	Si	Cl	Ca	K	Mg	N	O	Na	Cu	Be
<u>AlN:</u>											
Keramont	15.1	6.4	1.9	0.6	2.1	--	12.9	56.7	1.9	--	--
Norton	10.0	10.0	--	2.0	--	--	8.6	64.0	1.2	--	--
Hereaus	27.8	--	1.8	--	--	--	13.5	55.5	--	1.5	--
NTK	28.8	--	--	--	--	--	22.2	46.1	--	--	--
<u>Alumina:</u>											
90‡ NTK	5.7	22.8	--	--	--	--	2.1	67.8	--	--	--
96‡ Kyocera	11.6	15.6	--	0.8	--	--	2.4	68.0	--	--	--
96‡ Coors	22.7	10.5	--	1.1	--	--	2.7	62.2	--	--	--
96‡ NTK	31.0	4.6	--	--	--	1.1	2.1	60.6	0.4	--	--
<u>BeO</u>	--	3.5	--	--	--	--	4.1	58.8	0.9	--	24.7
<u>FC-01</u>	5.0	20.7	2.1	--	--	3.9	6.4	58.6	0.9	--	0.9

contaminants which now dominate the spectrum are silicon, nitrogen, and oxygen. Silicon could possibly come from the binders used in fabrication or from silicone lubricants used in the plastic bag which the samples were packaged in. Nitrogen and oxygen come from the atmosphere and adsorb on the surface, the amount depending on the age and reactivity of the surface.

Surface contamination also skewed the Auger results, as shown in Table 11. The AlN from Keramont is particularly dramatic with the substrate as received containing only carbon, nitrogen, and oxygen, but no aluminum signal. The combination of both a freon wash and a 30Å etch helped remedy this problem.

The changing dielectric constant for AlN, both quoted and calculated, is due more to a variation in porosity from manufacturer to manufacturer than is the case for alumina. The quoted densities vary from 3.2 g/cc for Hereaus to 3.8 g/cc for Norton. This variation is due to the difficulty in sintering AlN, as described previously. This new material is still in the research stage and companies are still "fine tuning" the amounts and types of sintering aids. Another consequence of this non-standard process is that the additives will also vary with manufacturer. The Auger and ESCA analysis confirm this.

FC-01 had the lowest dielectric constant, as was expected. It is a glass-ceramic composed of magnesia, alumina, and silica and is used primarily because of its superior dielectric properties.

7.2.2 Resistivity

All of the samples had a resistivity greater than 10^{15} ohm-cm when measured with a four point probe. They are all excellent insulators. Therefore, this property is not as much of a concern as are the others.

7.3 Mechanical Properties

Flexural strength and toughness are the two important mechanical properties of a packaging material. Therefore, the optimum experimental procedures would have been to do a 3 or 4-point bending test as well as impact testing. However, the size and quantity of samples along with the lack of appropriate equipment prevented these measurements. Instead, the elastic

Table 11 Compositional Analysis of Manufacturer Supplied Ceramic Packages
Using Auger Techniques

Sample	O	N	Atomic Percent Units for the Elements Detected									
			Ca	C	K	Cl	S	Si	Be(O)	Si(O)	Al	Al(O)
<u>AlN:</u>												
Keramont	12	32	--	19	--	--	8	--	--	--	37	--
Norton	29	12	--	21	--	--	--	--	--	--	30	--
Heraeus	24	16	--	24	--	--	--	--	--	--	34	--
NTK	15	31	--	14	--	--	--	--	--	--	40	--
<u>Alumina:</u>												
90‡ NTK	22	--	--	54	--	--	--	--	--	5	--	10
96‡ Kyocera	31	--	--	30	--	--	--	--	--	4	--	34
96‡ Coors	31	--	--	33	--	--	--	--	--	2	--	34
96‡ NTK	45	--	--	--	--	--	--	--	--	4	--	51
<u>BeO</u>	19	--	--	30	--	--	--	--	52	--	--	--
<u>FC-01</u>	48	--	--	12	--	--	--	--	--	40	--	--

modulus was measured using a DMA. The elastic modulus, in addition to grain size and defect concentration, is a good estimate of the mechanical integrity of the material.

The DMA measures the complex elastic modulus, E , defined by

$$E = E' + iE'' \quad (12)$$

where E' is the real part, known as the storage modulus, and E'' is the imaginary part, known as the loss modulus.

In the case of brittle ceramic materials, having little or no anelastic response, only the real part (the storage modulus) is of concern. For a properly run sample, the storage modulus of a ceramic should be approximately independent of temperature at moderate temperatures. In cases where the storage modulus was not constant, the most likely explanation is that the sample was not clamped as tightly as was necessary in the holder. The samples were so brittle that when the clamps were being tightened, the samples frequently broke. Once again, this test was very time consuming and equipment time was limited, making it difficult to test a statistically significant number of samples (only one sample of each was possible to test). Table 12 shows the measured values of elastic modulus compared to quoted values.

Table 12 Experimental Elastic Modulus Compared to Quoted Values

Sample	E (GPa)	
	Experimental (@25°C)	Quoted (T=?)
AlN(Norton)	525	281
AlN(Keramont)	170	281
AlN(Heraeus)	671	281
90% Al ₂ O ₃ (NTK)	363	276(Coors) 255(Kyocera)
96% Al ₂ O ₃ (NTK)	176	303(") 314(")
99.5% Al ₂ O ₃ (NTK)	401	372(") 363(")
FC-01	246	N/A
BeO	480	320-340
SiC	754	400

The relative experimental values of elastic modulus (at 25°C) are $E(\text{SiC}) > E(\text{AlN-Hereaus}) > E(\text{AlN-Norton}) > E(\text{BeO}) > E(90 \text{ percent alumina}) > E(99.5 \text{ percent alumina}) > E(\text{FC-01}) > E(96 \text{ percent alumina}) > E(\text{AlN-Keramont})$. As can be seen from the plots in Appendix D, the storage modulus of 96 percent alumina and AlN-Keramont were not constant. The samples must have not been clamped properly and the data is not very reliable.

Values of elastic modulus are seldom quoted by manufacturers, but the values found for flexural strength, S , show that $S(\text{AlN}) > S(\text{SiC}) > S(99.5 \text{ percent alumina}) > S(96 \text{ percent alumina}) > S(90 \text{ percent alumina}) > S(\text{BeO}) > S(\text{FC-01})$. These results again correspond to decreasing bond strength.

Deviations in flexural strength between like materials are due to microstructural differences such as grain size and porosity, which are a function of the original starting materials and processing conditions. Referring to the SEM photos, it can be seen in Figure 14 that FC-01 has a porous, multi-phase amorphous structure which accounts for its inferior mechanical properties. AlN shown in Figure 15 appears to have some sort of surface treatment. Alumina, Figure 16, has a slightly porous, uniformly small grain microstructure while BeO, Figure 17, has a very non-uniform large grain microstructure with few pores. The large grains of BeO contribute to its poor mechanical properties.

The method used for calculating density in this study was very crude with much error in the measurement of the sample's dimensions and lack of a sufficient number of samples for a statistical average. The results are reported in Table 13.

FIGURE 14. SEM Micrograph of FC-01

FIGURE 15. SEM Micrograph of AIN (NTK)

FIGURE 16. SEM Micrograph of Alumina (Coors)

FIGURE 17. SEM Micrograph of BeO

Table 13. Experimental Apparent Density Compared to Quoted Values.

Material	Density (g/cc)	
	Experimental	Quoted
AlN:		
Keramont	3.53	3.2-3.3
Norton	3.70/3.76	3.2-3.3
Hereaus	3.19	3.2-3.3
Al ₂ O ₃ :		
96% Kyocera	3.73/3.75	3.6-3.9
99.5% NTK	4.24	3.6-3.9
99.5% Coors	3.69	3.6-3.9
SiC	3.08	>3.1
FC-01	2.58	N/A
BeO	2.89	2.9

8. CONCLUSION

The important properties of a ceramic packaging material were identified to be the following: a high thermal conductivity, a low coefficient of thermal expansion, a low dielectric constant, a high dielectric strength, a low dielectric loss factor, high resistivity, high fracture strength, lightweight, and low cost.

Samples of commonly used materials (alumina, silicon carbide, aluminum nitride, beryllium oxide, and a glass ceramic composite) were obtained from ceramic manufacturers and evaluated in terms of the important parameters.

The composition and the amount and type of impurities were determining factors for the material's final thermal, electrical, and mechanical properties. Also an important factor was the processing procedure. This affects the density of the final product and thus a variety of properties. Finally, the testing conditions such as the ambient temperature range, sample preparation, and type of testing equipment further affected the values of the final properties. All of these factors accounted for the discrepancies between the same material from different manufacturers and in the measured and quoted values.

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APPENDIX A. EQUIPMENT USED TO EVALUATE PACKAGING MATERIALS

1. DuPont Model 981 DMA

1.1 DMA Schematic

1.2 DMA Sample Clamp Assembly

2. "X-Probe" ESCA (courtesy of Surface Science Labs)

**APPENDIX B. DATA AND CALCULATIONS FOR VARIOUS PROPERTIES OF CERAMIC
PACKAGING MATERIALS**

1. Determination of Dielectric Constant

1.1 Dielectric Constant (experimental)

Sample	Sample Thickness (mm)	Capacitance (fF) AVG s (n=15)	
96% Alumina (NTK)	0.52	43	1.5
99.5% Alumina (NTK)	0.60	35	3.1
AlN (NTK)	0.41	54	3.0
AlN (Norton)	0.58	32	1.9
AlN (Keramont)	0.75	17	2.6
AlN (Hereaus)	0.66	28	1.6
FC-01	0.66	5	3.2
BeO	0.65	12	2.0

$$\text{Area of probe} = \pi r^2 = \pi (18.5 \text{ mils})^2 = 1075.2 \text{ mils}^2 = 6.94 \times 10^{-3} \text{ cm}^2$$

The greatest value of capacitance was used because it is assumed to have the best contact.

$$C = kA\epsilon_0/d \quad \text{or} \quad k = dC/A\epsilon_0$$

where: C= capacitance k= dielectric constant
A= area of probe ϵ_0 = permittivity of free space

$$k(96\% \text{ alumina, NTK}) = \frac{(0.00052 \text{ m})(45 \times 10^{-15} \text{ F})}{(6.94 \times 10^{-7} \text{ m})(8.85 \times 10^{-12} \text{ F/m})} = 3.81$$

$$k(99.5\% \text{ alumina, NTK}) = \frac{(0.00060 \text{ m})(43 \times 10^{-15} \text{ F})}{(6.94 \times 10^{-7} \text{ m})(8.85 \times 10^{-12} \text{ F/m})} = 4.40$$

$$k(\text{AlN, NTK}) = \frac{(0.00041 \text{ m})(58 \times 10^{-15} \text{ F})}{(6.94 \times 10^{-7} \text{ m})(8.85 \times 10^{-12} \text{ F/m})} = 3.87$$

$$k(\text{AlN, Norton}) = \frac{(0.00058 \text{ m})(35 \times 10^{-15} \text{ F})}{(6.94 \times 10^{-7} \text{ m})(8.85 \times 10^{-12} \text{ F/m})} = 3.30$$

$$k(\text{AlN, Keramont}) = \frac{(0.00075 \text{ m})(24 \times 10^{-15} \text{ F})}{(6.94 \times 10^{-7} \text{ m})(8.85 \times 10^{-12} \text{ F/m})} = 2.93$$

$$k(\text{AlN, Hereaus}) = \frac{(0.00066 \text{ m})(32 \times 10^{-15} \text{ F})}{(6.94 \times 10^{-7} \text{ m})(8.85 \times 10^{-12} \text{ F/m})} = 3.44$$

$$k(\text{FC-01}) = \frac{(0.00066 \text{ m})(10 \times 10^{-15} \text{ F})}{(6.94 \times 10^{-7} \text{ m})(8.85 \times 10^{-12} \text{ F/m})} = 1.07$$

$$k(\text{BeO}) = \frac{(0.00065 \text{ m})(15 \times 10^{-15} \text{ F})}{(6.94 \times 10^{-7} \text{ m})(8.85 \times 10^{-12} \text{ F/m})} = 1.59$$

1.2 Comparison of Calculated Dielectric Constant with that Quoted by the Manufacturer

Sample	k(calc)	k(quoted by manufacturer)	DIFFERENCE
96% alumina (NTK)	3.81	9.3	5.49
99.5% alumina (NTK)	4.40	9.7	5.30
AlN (NTK)	3.87	9.0	5.13
AlN (Norton)	3.30	8.8	5.50
AlN (Keramont)	2.93	none quoted	
AlN (Hereaus)	3.44	none quoted	
FC-01	1.07	5.6	4.53
BeO	1.59	6.6	5.01

To account for the large difference in k values, the calculation must take a second capacitance, that of air, into consideration. Because of the awkwardness of the measurement configuration, the sample can tilt slightly between the probes, creating a gap. This gap must be taken into account as follows:

$$C(\text{total}) = 1/(1/C_1 + 1/C_2)$$

$$C(\text{total}) = 1/(t_1/k_1\epsilon_0 + t_2/k_2\epsilon_0)$$

$$k_2 = k(\text{air}) = 1$$

$$\epsilon_0 A = (8.85 \times 10^{-12})(6.94 \times 10^{-7}) = 6.14 \times 10^{-18} \text{ F-m}$$

$$t_2 = [1/C(\text{total}) - t_1/k_1\epsilon_0 A]\epsilon_0 A$$

CALCULATED AIR GAP THICKNESS RESULTING IN EXPERIMENTAL ERROR

SAMPLE	AIR GAP THICKNESS (t ₂)(mm)
96% Al ₂ O ₃ (NTK)	.081
99.5% Al ₂ O ₃ (NTK)	.081
AlN (NTK)	.060
AlN (Norton)	.110
FC-01	.490
BeO	.310

2. Determination of Specific Heat

$$C = Cp/m = \delta Q/m \delta T$$

where: C= specific heat m= mass
 Cp= heat capacity T= temperature
 Q= heat exchange

From the plots in Appendix C:

$$C = Y \times X/Z \times H$$

where:

Y= distance from the baseline to measurement(mm)

X/Y= unit measurement ((mcal/sec/mg)/mm)

H= heating rate (60 sec/10°C)

*specific heat calculated at 100°C

2.1 Specific Heats as Measured

AlN (Hereaus)

$$C = 28.36 \text{ mm} \times (.02 \text{ mcal/sec/mg})/13\text{mm} \times 6 \text{ sec/}^\circ\text{C} = .26 \text{ cal/g}^\circ\text{C}$$

AlN (Keramont)

$$C = 14.50 \text{ mm} \times (.02 \text{ mcal/sec/mg})/13\text{mm} \times 6 \text{ sec/}^\circ\text{C} = .13 \text{ cal/g}^\circ\text{C}$$

SiC

$$C1 = 8.0 \text{ mm} \times (.02 \text{ mcal/sec/mg})/13\text{mm} \times 6 \text{ sec/}^\circ\text{C} = .074 \text{ cal/g}^\circ\text{C}$$

$$C2 = \text{ " } \times \text{ " } \times \text{ " } = .074 \text{ cal/g}^\circ\text{C}$$

$$C3 = 8.5 \text{ mm} \times \text{ " } \times \text{ " } = .078 \text{ cal/g}^\circ\text{C}$$

$$C4 = 9.0 \text{ mm} \times \text{ " } \times \text{ " } = .083 \text{ cal/g}^\circ\text{C}$$

AlN (Norton)

$$C = 14.00 \text{ mm} \times (.02 \text{ mcal/sec/mg})/13\text{mm} \times 6 \text{ sec/}^\circ\text{C} = .13 \text{ cal/g}^\circ\text{C}$$

90% Alumina(NTK)

$$C = 18.0 \text{ mm} \times (.02 \text{ mcal/sec/mg})/13\text{mm} \times 6 \text{ sec/}^\circ\text{C} = .17 \text{ cal/g}^\circ\text{C}$$

FC-01

$$C = 69.5 \text{ mm} \times (.1 \text{ mcal/sec/mg})/13\text{mm} \times 6 \text{ sec/}^\circ\text{C} = 3.21 \text{ ca/g}^\circ\text{C}$$

BeO

$$C = 70.0 \text{ mm} \times (.06 \text{ mcal/sec/mg}) / 13 \text{ mm} \times 6 \text{ sec/}^\circ\text{C} = 1.94 \text{ cal/g}^\circ\text{C}$$

2.2 Specific Heats @100°C as Quoted by Manufacturers

MATERIAL	SPECIFIC HEAT (cal/g°C)
90% Alumina(Coors)	.22
94% "	.21
96% "	.21
99.5% "	.21
90% Alumina(Kyocera)	.20
92% "	.19
96% "	.19
99.5% "	.19

3. DETERMINATION OF ELASTIC MODULUS

3.1 Elastic Modulus (Experimental)

SAMPLE	*TENSILE STORAGE MODULUS(GPa)	TEMP(°C)
AlN (Norton)	540	-20
	525	25
	488	100
AlN (Keramont)	182	-20
	170	25
	142	100
AlN(Heraeus)	710	-20
	671	25
	639	100
90% Alumina (NTK)	380	-20
	363	25
	316	100
96% Alumina (NTK)	232	-20
	176	25
	173	100
99.5% Alumina (NTK)	418	-20
	401	25
	359	100
FC-01	359	-20
	246	25
	240	100
BeO	498	-20
	480	25
	428	100
SiC	754	25
	717	100

* FROM GRAPHS IN APPENDIX D.

3.2 Elastic Modulus as Quoted by Manufacturer

SAMPLE	E(GPa)
90% Alumina (Kyocera)	255
92% "	265
96% "	314
99.5% "	363
90% Alumina (Coors)	276
94% "	283
96% "	303
99.5% "	372
BeO	320-340
AlN	281
SiC	400

4. CALCULATION OF DENSITY

4.1 Density (Experimental)

AlN

Keramont:

$$1.7\text{ g} / (2.535\text{ cm} \times 2.535\text{ cm} \times .075\text{ cm}) = 3.53\text{ g/cc}$$

Norton:

$$0.59\text{ g} / (1.234\text{ cm} \times 2.54\text{ cm} \times .050\text{ cm}) = 3.76\text{ g/cc}$$

$$1.19\text{ g} / (2.530\text{ cm} \times 2.54\text{ cm} \times .050\text{ cm}) = 3.70\text{ g/cc}$$

Hereaus:

$$5.45\text{ g} / (5.084\text{ cm} \times 5.084\text{ cm} \times .066\text{ cm}) = 3.19\text{ g/cc}$$

Alumina

96% (Kyocera):

$$3.49\text{ g} / (2.162\text{ cm} \times 2.85\text{ cm} \times .151\text{ cm}) = 3.75\text{ g/cc}$$

$$1.77\text{ g} / (2.165\text{ cm} \times 1.453\text{ cm} \times .151\text{ cm}) = 3.73\text{ g/cc}$$

99.5% (NTK):

$$6.57\text{ g} / (5.085\text{ cm} \times 5.081\text{ cm} \times .060\text{ cm}) = 4.24\text{ g/cc}$$

99.5% (Coors):

$$44.15\text{ g} / (11.429\text{ cm} \times 9.524\text{ cm} \times .110\text{ cm}) = 3.69\text{ g/cc}$$

SiC

$$4.98\text{ g} / (5.103\text{ cm} \times 5.103\text{ cm} \times .062\text{ cm}) = 3.08\text{ g/cc}$$

FC-01

$$0.53\text{ g} / (1.300\text{ cm} \times 2.504\text{ cm} \times .063\text{ cm}) = 2.58\text{ g/cc}$$

BeO

$$1.20\text{ g} / (2.528\text{ cm} \times 2.528\text{ cm} \times .065\text{ cm}) = 2.89\text{ g/cc}$$

4.2 Quoted Density Values From Various Sources

AlN: 3.2-3.3 g/cc

Alumina: 3.6-3.9 g/cc

SiC: >3.1 g/cc

BeO: 2.9 g/cc

5. COMPOSITIONAL ANALYSIS

5.1 ESCA

5.1.1 Summary of ESCA Results

SAMPLE	Atomic Percent Units for the Elements Detected											
	Al	Si	Cl	C	Ca	K	Mg	N	O	Na	Cu	Zn
<u>AlN:</u>												
Keramont	5.6	2.4	0.7	63	0.6	0.8	--	4.8	21	0.7	--	--
Norton	2.5	2.5	--	75	0.5	--	--	3.0	16	0.3	--	--
Hereaus	15	--	1.0	46	--	--	--	7.3	30	--	0.8	--
NTK	15	--	--	48	--	--	--	12	24	--	--	--
<u>Al₂O₃:</u>												
90% NTK	1.6	6.4	--	72	--	--	--	0.6	19	--	--	--
96%	2.9	3.9	--	75	0.2	--	--	0.6	17	--	--	--
Kyocera												
96%	8.4	3.9	--	63	0.4	--	--	1.0	23	--	--	--
Coors												
96% NTK	22	3.3	--	29	--	--	0.8	1.5	43	0.3	--	--
<u>BeO</u>												
	--	1.2	--	66	--	--	--	1.4	20	0.3	--	8.
<u>EC-01</u>												
	2.9	12	1.2	42	--	--	2.3	3.7	34	0.5	--	0.5 --

5.1.2 ESCA Results After Normalizing for Carbon Contamination

<u>Atomic Percent Units for the Elements Detected</u>												
<u>SAMPLE</u>	Al	Si	Cl	Ca	K	Mg	N	O	Na	Cu	Zn	Be
<u>AlN:</u>												
Keramont	15.1	6.4	1.9	0.6	2.1	--	12.9	56.7	1.9	--	--	--
Norton	10.0	10.0	--	2.0	--	--	8.6	64.0	1.2	--	--	--
Hereaus	27.8	--	1.8	--	--	--	13.5	55.5	--	1.5	--	--
NTK	28.8	--	--	--	--	--	22.2	46.1	--	--	--	--
<u>Al₂O₃:</u>												
90% NTK	5.7	22.8	--	--	--	--	2.1	67.8	--	--	--	--
96% Kyocera	2.9	3.9	--	0.2	--	--	0.6	17	--	--	--	--
96% Coors	8.4	3.9	--	0.4	--	--	1.0	23	--	--	--	--
96% NTK	22	3.3	--	--	--	0.8	1.5	43	0.3	--	--	--
<u>BeO</u>	--	1.2	--	--	--	--	1.4	20	0.3	--	--	8.4
<u>FC-01</u>	2.9	12	1.2	--	--	2.3	3.7	34	0.5	--	0.5	--

5.2 SEM Micrographs

5.1.3 ESCA SPECTRA

A Res Power
 VERTICAL SCALE
 CURSOR BINDING ENERGY

ESCA SPECTRUM

SAMPLE:
 COMMENTS:
 A IN NORTON

DATE: 11/11/11
 DATA FILE # 1111

LOWER BINDING ENERGY (eV)
 Report # 1111

Resolution: 4

Spot: 600 u

Operator DS

Flux/Dan 2.0

Mag Primer

VE BIN AT 10.0

1000

COUNTS/IN

ESCA SPECTRUM

CURSOR BINDING ENERGY

binding energy (eV)
0.0
LOWER BINDING (eV)

DATE 11/27/1987
DATA FILE DAN3
Region 1

DISC: HARD

SAMPLE: AIN HCTIAEUS
COMMENTS:

Report # DAN
Spectrum #

5 | 5 | 0 SLANS

Resolution: 4

Spot: 600 u

Operator: DB

Flood Gun: 2.0

VERTICAL SCALE

4000

COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

DATE 11/27/1987

DATA FILE #DAN7

Region 1

DISC: HARD

SAMPLE COMMENTS

98X A1203 KYOCERA

1000.0
UPPER BINDING ENERGY (eV)

0.0
LOWER BINDING ENERGY (eV)

6 SCANS

Report #DAN8

SURFACE SCIENCE LABORATORIES 1700 10th Avenue Berkeley, CA 94704

DATE: 11/27/87

FILE: DAN7

REGION: 1

DISC: HARD

SCANS: 6

Resolution: 4

Spot: 600 U

Operator: DB

FloodGun: 2.0

VERTICAL SCALE

2000

COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

Report JDAW8

Spectrum 8: 6

SURFACE SCIENCE LABORATORIES 1704 Charleston Rd Mountain View California 94043 (415) 962 8767

Resolution: 4

Spot: 600 u

Operator: DS

FloodGun: 2.0

X-RayPower:

VERTICAL SCALE

1000

COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

SAMPLE

501.0

UPPER BINDING ENERGY (eV)

COMMENTS

90% Al2O3 NTK

Disc: HARD

DATE 11/27/1987

DATA FILE: DMS

Region 1

0.0

LOWER BINDING ENERGY (eV)

5 SCANS

Report # DAN

SURFACE SCIENCE LABORATORIES 1700 Chardston Rd Mountain View California 94043 (415) 947-8787

Spectrum # 1

Mag Power
 400
 COUNTS/INCH

Flood Gun 2.0

Operator DS

Spot: 600 u

Resolution: 4

ESCA SPECTRUM

CURSOR BINDING ENERGY

DATE 11/27/1987

DATA FILE DAN4

Region 1

HAPO

Report # DAN

Spectrum #

Illustration 4

Operator: [blank]

Flood Gun: [blank]

Beam: [blank]

Beam Power: [blank]

Vertical Scale

40000

Counts/Inc

ESCA SPECTRUM

CURSOR BINDING ENERGY

SAMPLE:

COMMENTS:

FC-01 NTK

A 10111111

DATE: 11/11/11

DATA FILE: JAN11

FILE: 11111

Report: 011111

Spectrum: 011111

SURFACE SCIENCE LABORATORIES 1700 Charleston Rd Mountain View CA 94043 (415) 962-8787

Resolution: 4

Spot: 600 u

Operator: DB

FloodGun: 2.0

Ray Power

VERTICAL SCALE

4000

COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

DATE 11/27/1987

DATA FILE #RANB

Region 1

Diag: HARD

SAMPLE: COMMENTS:

985 A1203 COOR8

1000.0

UPPER BINDING ENERGY (eV)

5

SCANS

Report #RANB

Spectrum #:

California 94043 (415) 962 8787

Mountain View

1208 Charleston Rd

SURFACE SCIENCE LABORATORIES

Report #RANB

Spectrum #:

California 94043 (415) 962 8787

Mountain View

1208 Charleston Rd

SURFACE SCIENCE LABORATORIES

5.3 EDX SPECTRA

QUANTEX-RAY GRAPHICS

AL2O3 COORS

Z=04 BE

PR= 100S

100SEC

O INT

V=2048 H=10KEV 1:10

AC=10KEV 10

0.16KEV

XES

QUANTEX-RAY GRAPHICS

FC-01 NTK

PR= 100S 100SEC

O INT

U=2048 H=1.0KEV 1:1Q AQ=1.0KEV 1Q

0.16KEV

XES

2.72KEV

QUANTEX-RAY GRAPHICS

ALN NTK

PR= 100S 100SEC 0 INT
U=8192 H=10KEV 1:10 AQ=10KEV 10

0.16KEV

XES

2..

QUANTEX-RAY GRAPHICS

BEO BRUSH WELLMAN

PR= 100S 100SEC

O INT

V=4096 H=10KEV 1:10

AQ=10KEV 10

0.16KEV

XES

2.7

5.4 SUMMARY OF AUGER RESULTS

Sample	O	N	<u>Atomic Percent Units for the Elements Detected</u>									
			Ca	C	K	Cl	S	Si	Be(O)	Si(O)	Al	Al(O)
AlN:												
Keramont	12	32	--	19	--	--	8	--	--	--	37	--
Norton	29	12	--	21	--	--	--	--	--	--	30	--
Heraeus	24	16	--	24	--	--	--	--	--	--	34	--
NTK	15	31	--	14	--	--	--	--	--	--	40	--
Alumina:												
90% NTK	22	--	--	54	--	--	--	--	--	5	--	10
96% Kyocera	31	--	--	30	--	--	--	--	--	4	--	34
96% Coors	31	--	--	33	--	--	--	--	--	2	--	34
96% NTK	45	--	--	--	--	--	--	--	--	4	--	51
BeO	19	--	--	30	--	--	--	--	52	--	--	--
FC-01	48	--	--	12	--	--	--	--	--	40	--	--

APPENDIX C. DSC CURVES USED IN THE DETERMINATION OF SPECIFIC HEAT

Sample: D/OF 428 G 340
 Size: 43.6 mg
 Run No: CSC-A1N-05
 Date: SEP/09/87 09:33

DSC (GRN)
 OMNITHERM DATA SYSTEM
 HEWLETT PACKARD DED

Operator: MB LANGE
 Disk ID: HP DED LAB
 File No: D 47.DAT V2.1
 Plotted: DEC/29/87 13:26

Sample: D/OF 429 G 340
 Size: 33 mg
 Run No: CSC-A1N-05
 Date: SEP/10/87 13:37

DSC (GRN)
 OMNITHERM DATA SYSTEM
 HEWLETT PACKARD DED

Operator: MB LANGE
 Disk ID: HP DED LAB
 File No: D 48.DAT V2.1
 Plotted: DEC/29/87 13:29

Sample: D/OF 448 & 340
 Size: 17.4 mg
 Run No: OSC-FC01-01
 Date: SEP/20/87 11:27

DSC (GRN)
 OMNITHERM DATA SYSTEM
 HEWLETT PACKARD QED

Operator: MB LANGE
 Disk ID: HP QED LAB
 File No: D 49.DAT V2.1
 Plotted: DEC/29/87 13:41

Sample: D/OF 478 & 340
 Size: 11.3 mg
 Run No: DSC-BeO-01
 Date: SEP/26/87 09:03

DSC (GRN)
 OMNITHERM DATA SYSTEM
 HEWLETT PACKARD QED

Operator: MB LANGE
 Disk ID: HP QED LAB
 File No: D 50.DAT V2.1
 Plotted: DEC/29/87 13:44

Sample: 007 488 S 340
 Date: SEP 14 97 07 25
 Size: 80.21 g
 Run No: 000-4-2000-05
 Date: SEP 14 97 07 25
 DTA SF 332 S 340
 99.5% Alumina (Coors)
 DSC 1000
 File No: 000-4-2000-05
 File No: 000-4-2000-05
 Date: SEP 26 97 11:05

Sample: D/OF 4 & 3
Size: 52.2 mg
Run No: DSC-A1N-10
Date: DEC/05/87 12: 21

DSC (GRN)
OMNITHERM DATA SYSTEM

Operator: MB LANGE
Disk ID: MARY
File No: D 11.DAT V2.1
Plotted: DEC/29/87 14: 11

Sample: D/OF 5 & 3
Size: 52.2 mg
Run No: DSC-A1N-10
Date: DEC/05/87 13: 57

DSC (GRN)
OMNITHERM DATA SYSTEM

Operator: MB LANGE
Disk ID: MARY
File No: D 12.DAT V2.1
Plotted: DEC/29/87 14: 14

Sample: D/OF 6 6 3
 Size: 52.2 mg
 Run No: DSC-A1N-10
 Date: DEC/08/87 14:23

DSC (GRN)

OMNITHERM DATA SYSTEM

Operator: MB LANGE
 Disk ID: MARY
 File No: D 13.DAT V2.1
 Plotted: DEC/29/87 14:17

Sample: D/OF 6 6 3
 Size: 28 mg
 Run No: DSC-SiC-01
 Date: DEC/12/87 09:16

DSC (GRN)

OMNITHERM DATA SYSTEM

Operator: MB LANGE
 Disk ID: MARY
 File No: D 15.DAT V2.1
 Plotted: DEC/29/87 14:24

APPENDIX D. DMA CURVES USED IN THE DETERMINATION OF ELASTIC MODULUS

AIN NORTON
HEWLETT PACKARD OED

TAN DELTA PEAK .003
PEAK TEMPERATURE -73.7°C
LOSS MODULUS PEAK 1.61E+00
PEAK TEMPERATURE -102.9°C

HEATING RATE 5 °C/MIN
FILE NAME HP0044
OPERATOR MB LANGE
TEST DATE 9/30/87

SILICON CARBIDE HEWLETT PACKARD OED

TAN DELTA PEAK .017
PEAK TEMPERATURE 134.7°C
SHEAR MODULUS PEAK 2.93E+10
PEAK TEMPERATURE 27.2°C

TENSILE MOD 0+25 7.54E+10
TENSILE MOD 0+100 7.17E+10

HEATING RATE 5 °C/MIN
FILE NAME HP0068
OPERATOR MARY BETH
TEST DATE 12/30/87

TAN DELTA PEAK .002
 PEAK TEMPERATURE 141.6°C
 LOSS MODULUS PEAK 8.74E+07
 PEAK TEMPERATURE -15.9°C

A1203 99.5% HEWLETT PACKARD OED

TENSILE MOD 0-55
 TENSILE MOD 0-20
 TENSILE MOD 0-25
 TENSILE MOD 0-100

LOG TENSILE LOSS MODULUS Pascals
 TAN DELTA

HEATING RATE 5 °C/MIN
 FILE NAME HP0056
 OPERATOR MB LANGE
 TEST DATE 10/9/87

TAN DELTA PEAK .099
 PEAK TEMPERATURE -118.8°C
 LOSS MODULUS PEAK 1.56E+08
 PEAK TEMPERATURE -114.3°C

96% A1203 HEWLETT PACKARD OED

HEATING RATE 5 °C/MIN
 FILE NAME HP0051
 OPERATOR MB LANGE
 TEST DATE 10/3/87

TAN DELTA PEAK .002
 PEAK TEMPERATURE 150.7°C
 LOSS MODULUS PEAK 4.44E+07
 PEAK TEMPERATURE -121.4°C

90% A1203 NTK
HEWLETT PACKARD OED

TENSILE MOD 0-55 3.69E+10
 TENSILE MOD 0-20 3.08E+10
 TENSILE MOD 0-25 3.63E+10
 TENSILE MOD 0-100 3.16E+10

AIN HERAEUS
HEWLETT PACKARD OED

TAN DELTA PEAK .003
PEAK TEMPERATURE 170.2°C
LOSS MODULUS PEAK 1.26E+08
PEAK TEMPERATURE 170.2°C

TENSILE MOD 0-55 7.56E+10
TENSILE MOD 0-20 7.10E+10
TENSILE MOD 0-25 6.71E+10
TENSILE MOD 0-100 6.39E+10

HEATING RATE 5 °C/MIN
FILE NAME HP0046
OPERATOR MB LANGE
TEST DATE 9/30/87

LOSS MODULUS PEAK 9.19E+06
PEAK TEMPERATURE -65.6°C

AIN KERRMONT HEWLETT PACKARD OED

TENSILE MOD 0-55 1.72E+10
TENSILE MOD 0-20 1.82E+10
TENSILE MOD 0-25 1.70E+10
TENSILE MOD 0-100 1.42E+10

HEATING RATE 5 °C/MIN
FILE NAME HP0042
OPERATOR MB LANGE
TEST DATE 9/29/87