

Better ceramic substrates through zeolites

M A SUBRAMANIAN, D R CORBIN and U CHOWDHRY*

E. I. duPont de Nemours and Company, Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0328, USA

*Current address: Jackson Laboratory, E. I. du Pont de Nemours and Company, Chambers Works, Deepwater, New Jersey 08023, USA

Abstract. A novel synthetic route for fabricating dense aluminosilicate-based ceramics at relatively low temperatures ($\leq 1000^\circ\text{C}$) is described. The method involves ion exchange of an appropriate zeolite powder, followed by fabrication and sintering, to form a dense ceramic. Anorthite, cordierite- and β -spodumene-based ceramic substrates with attractive physical properties for microelectronic packaging are obtained using these unusual precursors. A brief overview on the property requirements for substrates used in microelectronic packaging is outlined at the beginning of the article.

Keywords. Zeolites; precursors; ceramics; microelectronic packaging; anorthite; cordierite.

1. Introduction to microelectronic packaging

The continuing desire for faster and denser electronic microcircuits leads to challenges in the design of substrate materials on both the atomic and micron scales. This section will review the materials and processing requirements for ceramic substrates used in microelectronic packaging. The integrated circuitry (IC) on a silicon chip is the central component of all logic and memory functions on which today's computers and other electronic systems are based. The term microelectronic packaging refers to the assembly of functions that support, protect, provide power to, and transmit signals from the IC chip (Harper and Staley 1985; Chowdhry and Sleight 1987). A schematic diagram of a multilayer package is shown in figure 1 depicting several insulating layers of a ceramic-glass thick film paste screen printed and sintered onto a rigid alumina substrate. The chip is bonded to the top insulating layer that also houses various conducting circuit patterns. Interconnections to the patterns in the layers below are provided by 'via holes'.

Important substrates for electronic interconnection may be broadly divided into three major categories: ceramic-based, polymer-printed circuit-board-based, and structures built up on a metal core. For high performance packages in which thermal stability and impermeability are essential, ceramic-based packages are preferred over plastics (Wilcox 1971; Schwartz 1984a; Tummala 1988). The industry trend in ceramic packages is toward cofired multilayer structures that involve casting ceramic tape, metallization, lamination, and simultaneous sintering of the insulating layer and conducting components (Schwartz 1984b). The substrate material most widely used today is alumina ($\alpha - \text{Al}_2\text{O}_3$) which is traditionally sintered at 1600°C . This high sintering temperature necessitates the use of refractory metals such as Mo and W to form the conducting patterns. The material of choice for future conductors is Cu because of its high conductivity and low cost. However, the use of Cu requires a ceramic system that sinters to high density below 1000°C in a non-oxidizing atmosphere.

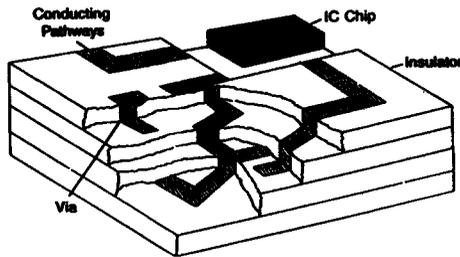


Figure 1. Schematic diagram of a multilayer ceramic microelectronic package.

Table 1. Property requirements of substrates for electronic packaging.

Low dielectric constant
Low dielectric loss
High dielectric strength
High electrical resistivity
Thermal expansion match with silicon chip ($3.5 \times 10^{-6}/^{\circ}\text{C}$)
Good mechanical strength
Surface smoothness
Hermetic
Low-temperature processability
Stable
Non-toxic
Low cost

1.1 Substrate properties

The property requirements of substrate materials for microelectronic packaging are listed in table 1.

1.1a *Dielectric properties:* The two parameters of transmission line conductors of most importance in designing high speed circuitry are velocity of propagation and characteristic impedance (Harper and Staley 1985). Both are related to the dielectric constant of the substrate. The time delay for signal propagation is given by

$$t_d = \sqrt{\frac{\kappa l}{c}}, \quad (1)$$

where κ is the dielectric constant of the substrate, l the distance the signal must travel, and c the velocity of light.

Hence, the dielectric constant of the substrate should be as low as possible. The highest velocity of propagation is obtained for a conductor surrounded by air or vacuum with a dielectric constant of 1.0. With high speed devices, it is important to match the transmission line impedance to the specific device input impedance. In addition to dielectric constant, conductor line width and dielectric thickness must be controlled for impedance matching (Harper and Staley 1985).

The lowest dielectric constants will generally occur for highly covalently bonded materials with low atomic number. Thus, certain organic materials would be preferred as substrates if dielectric properties were the only consideration. Glasses can have

desirable dielectric properties, but they have inferior mechanical strength and thermal conductivity.

Dielectric losses ($\tan \delta$) in materials occur at various frequencies and are related to various polarization mechanisms (von Hippel 1954). Generally, these loss peaks must be avoided. Dielectric losses greater than 0.005 are usually considered unacceptable for substrate applications since dielectric loss results in conversion of electrical energy into heat.

The electrical resistivities of the substrate should be very high, greater than 10^{12} ohm-cm at ambient temperatures, so that there is little chance of current leakage between conductor lines. Presence of mobile cation impurities such as Na, K, Li, Cu or Ag at significant levels should be avoided since they can degrade the insulation resistance (Schwartz 1984a).

1.1b *Thermal conductivity*: Conventional circuits are air cooled for power densities up to 1 W/cm^2 . For high speed circuits, liquid cooling techniques extend cooling capacity to 20 W/cm^2 . Ceramic substrates can serve as a heat sink and are therefore preferred over polymer-based substrates for high performance circuits (Wilcox 1971).

1.1c *Thermal expansion*: During device assembly and use, thermal cycling can cause cracks to form in the solder joints often used to connect the chip to the ceramic substrate. To prevent chip detachment and device failure, it is important to match the thermal expansion coefficient of the substrate to that of Si (Wilcox 1971).

The list of desired properties for an ideal substrate material is formidable (table 1). The best candidates are covalent compounds of the light elements, and these are generally difficult to process. No one compound possesses all the desired properties for a substrate. Thus, different substrate materials are used depending on the specific application for the microelectronic package. If the overriding consideration is high speed, the emphasis will be on substrates with a dielectric constant of 3 or less. No dense inorganic material can achieve such a low κ , but inorganic materials containing high porosity are under very active consideration. The porosity must be closed in order to achieve hermeticity.

Materials with very low dielectric constant have relatively poor thermal conductivity; thus, heat must be dissipated in a manner not dependent on the substrate as a heat sink: In a high power application, the substrate must act as a very good heat sink. The material of choice in this case has been BeO which will probably be replaced by AlN due mainly to the toxicity of Be (table 2).

1.2 *Aluminosilicate-based ceramics as substrates*

Aluminosilicates offer certain advantages for use as packaging materials. Many aluminosilicate-based ceramics such as cordierite ($2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) (Genesse and Chowdhry 1986), anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) (Gdula 1970; Hayashi and Fukui 1980) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) (Mussler and Shafer 1984) have attracted attention in recent years as alternative substrate materials to conventionally used α -alumina. They offer the advantages of lower dielectric constants and lower thermal expansion coefficients than those of alumina (table 2). They also offer the potential for lower sintering and densification temperatures than conventionally used for α -alumina

Table 2. Dielectric and thermal properties of selected substrate materials.

	Dielectric constant κ	Thermal expansion $\alpha \times 10^{-6}/^{\circ}\text{C}$ (25–400°C)	Thermal conductivity W/m K
Diamond	5.7	1.5	2000
SiC	40	3.7	490
Si ₃ N ₄	6.0	3.0	30
AlN	8.8	4.5	320
BeO	6.9	9.0	370
Al ₂ O ₃	9.6	7.8	30
SiO ₂ (quartz)	4.3	10–12	7
SiO ₂ (glass)	3.8	0.55	2
B/Si/O (glass)	4.1	3.3	1.8
Hexagonal cordierite (2MgO·2Al ₂ O ₃ ·5SiO ₂)	5–6	1–2	1–2
Mullite (3Al ₂ O ₃ ·2SiO ₂)	6.6	5.5	$\bar{3}$
Anorthite (CaO·Al ₂ O ₃ ·2SiO ₂)	7.0	4.8	2
β -Spodumene (Li ₂ O·Al ₂ O ₃ ·4SiO ₂)	6.5	2.1	2
Polyimide	2.2	20–50	0.2

(1600°C). However, traditional processing involves the melting of the appropriate oxides at generally >1400°C, quenching to form a glass, and subsequent crystallization by a controlled heat treatment.

The cordierite family of glass-ceramics has a dielectric constant (5–6 at 1 MHz) lower than that of Al₂O₃ and potential for attractively low sintering temperatures. The average thermal expansion coefficient of cordierite is, however, very low (table 2). It has been shown (Mussler and Shafer 1984) that addition of mullite to cordierite allows tailoring of the thermal expansion coefficient of the composite. Thus, a composite consisting of 65 vol% cordierite and 35 vol% mullite has a thermal expansion coefficient matching that of Si.

1.2a Ceramic processing: Having identified a material or combination of materials that satisfies the requirements described above, the next challenge is to process it into a dense, hermetic body of the desired shape below 1000°C. In general, materials with strong covalent bonding that are desirable for their high thermal conductivity, low dielectric constant and low expansivity have low diffusivities and do not sinter readily (Chowdhry and Sleight 1987). From a practical standpoint, either reactive liquid phase sintering or viscous flow rather than solid state diffusion are the mechanisms adopted for processing of electronic ceramics. The processing of ceramics below 1000°C generally involves a liquid phase or viscous sintering mechanism. Control over the size distribution and packing of the particles prior to sintering as well as control over the system viscosity is essential to achieve a dense substrate at relatively low temperatures. During sintering, grain growth must be minimized because fine grained ceramics are needed for the smooth surfaces required for high resolution circuit patterns. Processing flaws must be minimized to achieve good mechanical properties. In addition, the systems selected should be stable, non-toxic and relatively inexpensive.

2. Zeolites as precursors to ceramic substrate materials

Ceramics have traditionally been made by shaping natural or man-made powders into objects and subsequently densifying them. One of the major thrusts in recent ceramics research has been directed toward the development of materials with greatly improved mechanical reliability by improving the properties of the ceramic precursor. The conventional way of making fine powders is to grind a bulk material and pass it through a fine sieve. Although fine powders may result, they may not be uniform in size and grinding the material may introduce impurities. One method for preparing pure, superfine, uniform-sized powders is the sol-gel process (Zelinski and Uhlmann 1984; Roy 1987). The sol-gel method involves the conversion of a sol to a gel and subsequent drying. Although the sol-gel method offers a number of advantages over other techniques, such as better homogeneity because of mixing on the atomic scale, higher purity, uniform small particle size, and lower temperature of preparation, it does have a number of disadvantages. These include high cost of raw materials, large shrinkage during processing, residual fine pores, residual hydroxyls, residual carbon, health hazards of organic solutions, and long processing times.

Zeolites are crystalline aluminosilicate materials with open framework structures. Zeolites may be generally represented by the formula $M_{2/n} \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$, where M is a cation of valence n , x is generally greater than or equal to 2, and y can vary from 0 to 10. There are approximately 40 naturally occurring zeolites and over 100 synthetic forms (Breck 1984; Thomas and Catlow 1987; Dyer 1988). The synthetic forms are crystallized from aluminosilicate gels containing alkali metals. These alkali cations can generally be easily replaced by conventional ion-exchange of the crystalline zeolite. This ion-exchange ability allows homogeneous compositional variations on the atomic scale. As a result of properties such as high surface area, ion exchange capacity and molecular sieving ability, zeolites have found application in cracking, separations, drying and in detergent formulations. Several varieties (e.g. zeolites A, X and Y) are commercially available in large volumes at relatively low cost. Table 3 lists the composition of zeolites A, X and Y, which are available commercially. The sodium in these zeolites can be replaced by other monovalent cations such as Li or K; by divalent cations such as Mg, Ca, Sr, Ba or Pb; or by mixtures of cations, to the extent that charge neutrality is maintained. Many of the synthetic zeolites have compositions close to those of the desired aluminosilicate-based ceramics listed in table 4. The ion-exchange ability of zeolites allows homogeneous compositional variation on an atomic scale. This advantage, coupled with their uniform particle size and low cost, make zeolites very attractive precursors to aluminosilicate-based ceramics.

Table 3. Compositions of commercial zeolites.

Zeolite*	Composition
Linde 4A	$Na_{12}Al_{12}Si_{12}O_{48} \cdot xH_2O$
Linde 13X	$Na_{86}Al_{86}Si_{106}O_{384} \cdot xH_2O$
Linde LZ-Y52	$Na_{56}Al_{56}Si_{136}O_{384} \cdot xH_2O$

*All zeolites obtained from Alfa Products Div., Danvers, MA, USA

Table 4. Zeolite stoichiometry similar to desired ceramics.

Zeolite	Composition	Ceramic composition
Ca-A	$\text{Ca}_6\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$	$6\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite)
Ca-X	$\text{Ca}_{43}\text{Al}_{86}\text{Si}_{106}\text{O}_{384}$	$43\text{CaAl}_2\text{Si}_2\text{O}_8 + 20\text{SiO}_2$
Mg-Y	$\text{Mg}_{28}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$	$14\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (cordierite) + 66SiO_2
Li-A	$\text{Li}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$	$12\text{Li}_{1-x}\text{Al}_{1-x}\text{Si}_{1+x}\text{O}_4$, $x = 0$ (β -eucryptite)
Li-Y	$\text{Li}_{56}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$	$56\text{Li}_x\text{Al}_x\text{Si}_{1-x}\text{O}_2$, $x = 0.29$ (β -spodumene)
Ba-A	$\text{Ba}_6\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$	$6\text{BaAl}_2\text{Si}_2\text{O}_8$ (celsian)

In this section, we describe a novel route, namely the use of ion exchanged zeolites as precursors, to aluminosilicate-based ceramic substrates for microelectronics packaging applications.

2.1 Preparation and characterization of zeolite precursors and ceramics

Zeolites 4A (Na-A), 13X (Na-X), and LZ-Y52 (Na-Y) were exchanged by conventional ion exchange techniques with the various cations described in the text, generally using nitrate salts. The dry, exchanged zeolite powder was ground in an agate mortar for 15 min and then pressed into 13 mm pellets at 97 MPa. The pellets were then heated at 1°C/min to the desired temperature and held there for 3 h. Shrinkage was measured with an Orton dilatometer. The density was determined using conventional techniques and with a helium autopycnometer. Hermeticity was determined by a dye penetration and a water absorption test. Dielectric properties were measured on sintered disks with sputtered gold electrodes. The capacitance and loss angle were measured at 1 MHz using an HP 4275A LCR bridge and the dielectric constant, κ , was calculated using the formula $\kappa = ct/\epsilon_0 A$, where t is the sample thickness, A the electrode area, and ϵ_0 the permittivity constant. The resistivity was measured using a Keithley 617 electrometer. The coefficient of linear thermal expansion was measured using an Orton dilatometer in the range 25° to 400°C. X-ray powder diffraction data were obtained using a Phillips APD 3600, a Phillips APD 3700, or a Scintag PAD-5 diffractometer.

2.2 Anorthite-based ceramics from Ca-X zeolites

A series of Ca-exchanged Na-A, Na-X and Na-Y zeolites with varying Si/Al contents was prepared using the ion-exchange technique (Subramanian *et al* 1989). These zeolites were converted to anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) as follows:



Virtually no shrinkage occurs up to 700°C. This is a desired processing advantage from the point of view of binder removal (Subramanian *et al* 1989). The pores in the

material remain open to high enough temperatures that complete binder removal is effected. At 750°C, a sharp change in sample dimensions, characteristic of liquid phase sintering, is revealed. Zeolites are metastable materials, whose structure collapses above a certain temperature. The X-ray diffraction patterns (figure 2) indicate that at 800°C, the material is still crystalline Ca-X zeolite. By 850°C, the structure has collapsed, and the material is now completely amorphous. Above 900°C, anorthite has recrystallized from the glassy matrix. At 950°C, the sample is dense and hermetic.

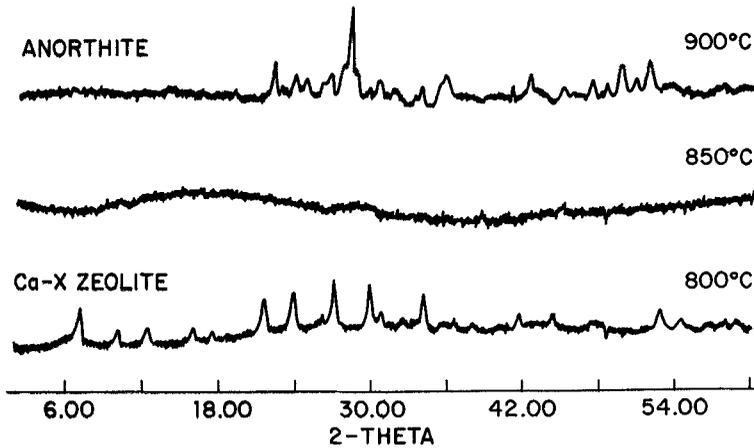


Figure 2. X-ray diffraction data showing the formation of an anorthite phase at 900°C from Ca-X zeolite.

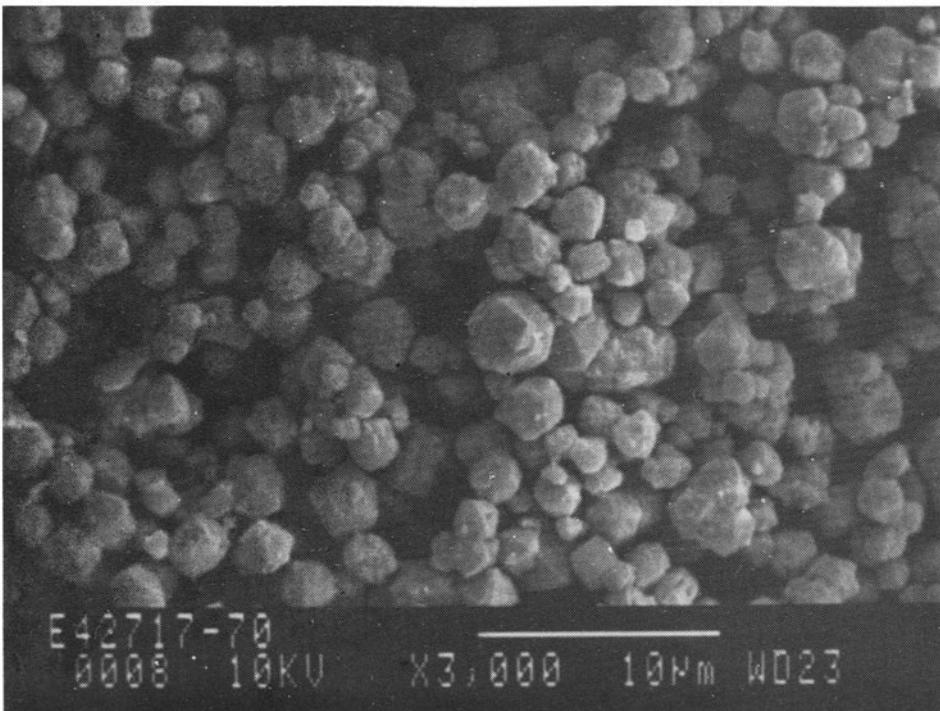


Figure 3. Scanning electron micrograph of Ca-X zeolite powder.



Figure 4. Scanning electron micrograph of anorthite-based ceramics from Ca-X zeolite: (a) surface and (b) cross section.

The process sequence from crystalline to amorphous to crystalline material is desirable for low temperature sintering and densification. Figure 3 indicates the nature of the powder packing for Ca-X zeolite prior to firing. The particle size distribution and the pore size distribution are relatively narrow. When heated, the material is densified by viscous flow. It is desirable to achieve complete densification of the material in the glassy state prior to crystallization. The fired microstructures (figures 4a and b) show a dense surface and a fracture surface, with a few isolated pores. If the heating schedule is optimized, complete densification can be achieved in the glassy state. Recrystallization of the glass to form anorthite is accompanied by $\approx 40\%$ volume change, but this change is not significant enough to cause cracking (Subramanian *et al* 1989). The final average grain size of the anorthite formed after crystallization is $< 1 \mu\text{m}$.

The properties of the sintered material prepared from Ca-X are shown in table 5. The densification temperature of 900°C is attractively low. The dielectric constant at 1 MHz is 6.5, with a low loss of 6×10^{-4} . The dielectric constant can be lowered if excess silica is used, but this lower value does cause mechanical properties to degrade. The linear thermal expansion coefficient of the anorthite made from Ca-X is $4.2 \times 10^{-6}/^\circ\text{C}$, a very close match to that of Si (table 1).

In the preparation of anorthite from zeolite precursors, the alkali metal containing zeolite can be first exchanged with ammonium nitrate to give the ammonium form of the zeolite. This step is incorporated into the preparation to help guarantee the removal of undesired alkali ions that can seriously affect the dielectric properties of the resulting ceramic (Corbin *et al* 1991). The effect of residual sodium in the zeolite on the dielectric loss of anorthite ceramics derived from Ca-X zeolite is illustrated in figure 5. In this example, only after about 95% of the sodium has been removed does the dielectric loss fall below the maximum desired level (0.001).

2.3 Anorthite-cordierite-based composite ceramics from Ca, Mg-X zeolites

Although anorthite is a very attractive material for electronic packaging itself, superior properties are found in a composite of anorthite and hexagonal cordierite. Adding hexagonal cordierite to anorthite lowers the dielectric constant further, causing a better match of the thermal expansion coefficient to that of Si.

Table 5. Anorthite-based ceramic substrate properties (from Ca-X zeolite).

Composition (wt%)	
CaO	14.94
Al ₂ O ₃	33.22
SiO ₂	51.21
Na ₂ O	0.63
Sintering temperature	900°C
Density	> 98%
Water absorption	0%
Dielectric constant (κ)	6.5
Dielectric loss	0.0006
Insulation resistant ($\Omega \cdot \text{cm}$)	$> 10^{13}$
Thermal expansion/ $^\circ\text{C}$	4.2×10^{-6}

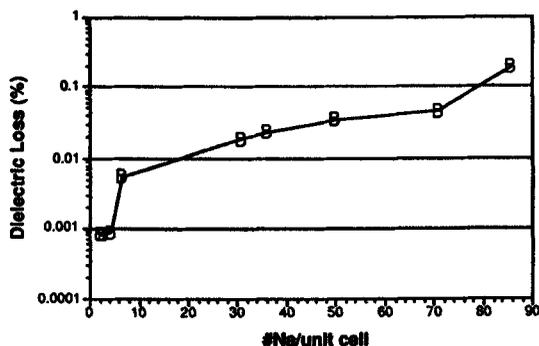


Figure 5. Effect of residual sodium content on the dielectric loss for anorthite ceramics derived from Ca-X zeolite sintered at 1050°C.

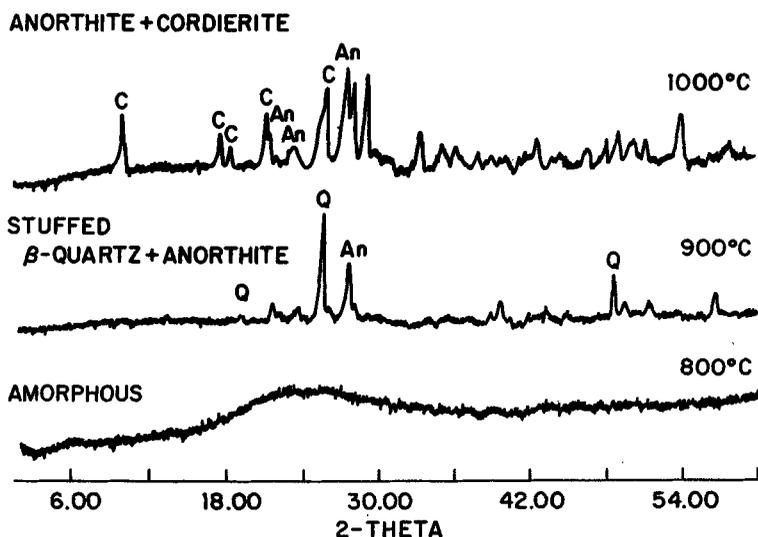


Figure 6. X-ray diffraction data showing the formation of anorthite-cordierite-based composite ceramic from Ca, Mg-X zeolite.

A suitable zeolite precursor for anorthite-cordierite-based ceramics was prepared by partial exchange of Mg for Ca in Ca-X, as described earlier. Chemical analysis of the precursor powder showed that $\approx 50\%$ of Ca in Ca-X was replaced by Mg. The precursor powder had a narrow particle size distribution of 1 to 4 μm . The above-mentioned powder in pellet form was heated to various temperatures in the range 700° to 1400°C. The XRD patterns (figure 6) show that at 800°C the structure collapses and the material is completely amorphous. At 900°C, in addition to anorthite, formation of a stuffed β -quartz type phase is noted. With further heating to 1000°C, the stuffed β -quartz converts to cordierite, and with this conversion the dielectric constant decreases significantly. In table 6, a summary of the phases formed and dielectric properties of Mg, Ca-X zeolite sintered at various temperatures is given.

The properties of $\alpha\text{-Al}_2\text{O}_3$, anorthite prepared from Ca-X; anorthite-cordierite composites prepared from Ca, Mg-X; and cordierite prepared from Mg-Y are compared in table 7. This comparison clearly shows that aluminosilicate-based ceramics

Table 6. Summary of phases formed and dielectric properties of Mg, Ca-X (~ 50% Mg exchanged)* zeolite sintered at various temperatures.

Sintering temp. (°C)	Phases formed†	Dielectric constant κ , at 1 MHz	Dielectric loss $\tan \delta$ at 1 MHz
900	Anorthite (30) + β -Quartz (70)	7.9	0.0005
1000	Cordierite (45) + Anorthite (30) + β -Quartz (25)	5.8	0.0009
1050	Cordierite (55) + Anorthite (30) + β -Quartz (15)	5.5	0.0010
1200	Cordierite (65) + Anorthite (30) + β -Quartz (5)	5.3	0.0009
1300	Cordierite (70) + Anorthite (30)	5.2	0.0005
1400	Mullite + Glass	—	—

*Chemical composition: $\text{Ca}_{17}\text{Mg}_{22}(\text{NH}_4)_3\text{NaAl}_{86}\text{Si}_{106}\text{O}_{384} \cdot x\text{H}_2\text{O}$.

†Mol% of phases formed are given in parentheses.

Table 7. Electrical and thermal properties of anorthite- and cordierite-based ceramics derived from zeolites. Values for alumina ceramic are given for comparison.

Ceramic	Dielectric constant κ at 1 MHz	Dielectric loss $\tan \delta$ at 1 MHz	Resistivity (ohm-cm)	Thermal expansion ($\times 10^{-6}/^\circ\text{C}$)	Sintering temp. ($^\circ\text{C}$)
An-X*	6.6	0.0006	$> 10^{13}$	4.4	900
An-Cor-X†	5.6	0.0009	$> 10^{13}$	3.3	1000
Cor-Y††	5.2	0.0020	$> 10^{12}$	2.1	1050
Al_2O_3	9.6	0.0002	$> 10^{14}$	7.8	1500

*An-X, anorthite obtained from Ca-X zeolite.

†An-Cor-X, anorthite-cordierite from Ca, Mg-X zeolite.

††Cor-X, cordierite from Mg, NH_4 -Y zeolite.

prepared from zeolites have desirably lower sintering temperatures, lower dielectric constants and lower thermal expansion coefficients compared to conventionally used α -alumina. The α -alumina substrates would, however, have a higher thermal conductivity, as well as higher mechanical strength and toughness.

2.4 Cordierite-based ceramics from Mg, NH_4 -Y zeolites

Sintering of Mg, NH_4 -Y (Mg: $\text{NH}_4 = 2.2$, 1.73% residual Na_2O) at 1100°C resulted in a dense, cordierite-based ceramic with a dielectric constant of 5.2, a dielectric loss of 0.002, volume resistivity of 10^{12} ohm-cm and a coefficient of thermal expansion of $2.1 \times 10^{-6}/^\circ\text{C}$ (table 7).

2.5 β -Spodumene and β -eucryptite ceramics from Li-exchanged zeolites

Firing of Li-A (2.62% residual Na_2O) and Li-X (2.64% residual Na_2O) zeolites at 1050°C gives β -eucryptite as the major component. Li-X when heated to 1200°C converts to a β -spodumene related solid solution. At 700°C, zeolite Li-Y (3.36% residual Na_2O) is transformed into an amorphous phase and upon further heating to 800°C formation of lithium aluminosilicate with high-quartz structure is observed. When

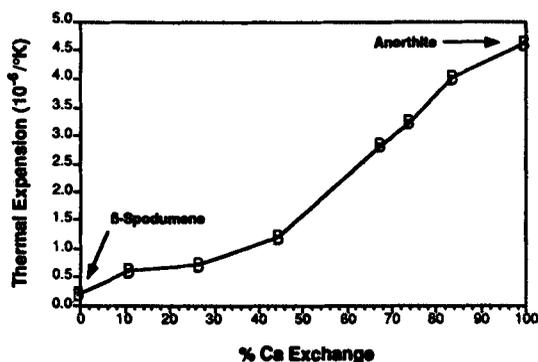


Figure 7. Effect of degree of calcium exchange on coefficient of thermal expansion for β -spodumene/anorthite composites derived from Li, Ca-Y zeolites sintered at 1000°C.

Table 8. Other ceramics from zeolites.

Zeolite	Ceramic (1050°C)
Ba-A, Ba-X, Ba-Y	BaAl ₂ Si ₂ O ₈ (celsian)
Pb-A, Pb-X, Pb-Y	PbAl ₂ Si ₂ O ₈
NH ₄ -A, NH ₄ -X, NH ₄ -Y	Al ₆ Si ₂ O ₁₃ (mullite)
Zn-A, Zn-X, Zn-Y	ZnAl ₂ O ₄
Mg, NH ₄ -A; Mg, NH ₄ -X	MgAl ₂ O ₄ (spinel), Al ₆ Si ₂ O ₁₃ (mullite)
Na-A, Na-X, Na-Y	NaAlSi ₃ O ₈ (albite)
K-A, K-X, K-Y	KAlSi ₂ O ₆

heated above 900°C, the high-quartz structure is transformed into a β -spodumene related solid solution. X-ray and MASNMR studies (Subramanian *et al* 1986) indicate that the β -spodumene solid solution has a composition close to $(\text{Li}_{0.23}\text{Na}_{0.06})\text{Al}_{0.29}\text{Si}_{0.71}\text{O}_2$, which is in agreement with chemical analysis.

2.6 β -Spodumene/anorthite ceramics from Li, Ca-Y zeolites

Sintering of Li, Ca-Y zeolites with varying amounts of calcium results in β -spodumene/anorthite composites as determined by X-ray powder diffraction. The addition of calcium results in improved dielectric loss (0.001 for Li, Ca-Y vs 0.01 for Li-Y) and the ability to vary the thermal expansion coefficient by varying the calcium content. This is shown in figure 7.

2.7 Other ceramics from zeolites

Some of the other ceramics prepared from zeolites as precursors are listed in table 8. Generally, aluminosilicate materials are obtained; however, it is interesting that for the smaller ions magnesium and zinc, the aluminate is formed instead of the aluminosilicate. In the case of the Mg-exchanged zeolites at 900 to 1050°C, a mixed phase material is obtained containing spinel and mullite. It is reported that Mg-X gives cordierite under more severe conditions, i.e. after glass formation at 1500°C and heating at 1000°C (Breck 1984).

3. EXAFS characterization of the transformation of zeolites to aluminosilicate ceramics

The decomposition of zeolite precursors is a novel route for the preparation of aluminosilicate-based substrate materials (Subramanian *et al* 1986, 1989; Chowdhry *et al* 1989; Parise *et al* 1989; Bedard and Flanigen 1990; Corbin *et al* 1991). While the structural reconstruction of zeolites to more dense phases is known, little is understood of the mechanism of this process. Studies of structural rearrangement in a variety of solid state materials is often hampered by the intermediate's lack of long range order (crystallinity). In these cases the traditional techniques of X-ray and neutron powder crystallography give way to the spectroscopies. EXAFS (extended X-ray absorption fine structure) offers the opportunity to compare crystalline starting materials, where geometries are well characterized, with amorphous intermediates to decide whether the whole process is reconstructive or whether certain elements of structure are retained during the transition. We have examined the reconstructive transition from Sr-A zeolite, through X-ray amorphous intermediates, to Sr-anorthite by EXAFS and have shown that the environment around the strontium remains essentially intact (Parise *et al* 1989). The strontium is coordinated near a flat 6-ring in Sr-A, sandwiched between a double 6-ring in Sr-hexacelsian, and between layers in Sr-anorthite. Although the intermediate amorphous materials produced at 850°C and 900°C have quite similar X-ray powder patterns, they have very different EXAFS spectra. The Fourier transform for the 850°C sample is very similar to that of dehydrated Sr-A, the 900°C sample is more similar to Sr-hexacelsian. These similarities can be explained if the primary coordination about the Sr in Sr-A is maintained.

4. Summary

Zeolites offer promise as precursors to aluminosilicate-based ceramics: they are readily synthesized, with a narrow particle size distribution, and can be obtained at low cost. Their ion exchange properties allow a wide range of possibilities for the precursor composition. When heated, zeolites become amorphous and densify at relatively low temperatures, by viscous flow prior to crystallization to the desired ceramic. The dielectric and thermal expansion properties, in addition to the processing advantages, make anorthite and anorthite-cordierite composite ceramics prepared from zeolite precursors very attractive substrate candidates for use in microelectronic packaging.

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