Kirk-Othmer Encyclopedia of Chemical Technology.

ADVANCED CERAMICS, ELECTRONIC CERAMICS

Electronic ceramics is a generic term describing a class of inorganic, nonmetallic materials utilized in the electronics industry. Although the term electronic ceramics, or electroceramics, includes amorphous glasses and single crystals, it generally pertains to polycrystalline inorganic solids comprised of randomly oriented crystallites (grains) intimately bonded together. This random orientation of small, micrometer-size crystals results in an isotropic ceramic possessing equivalent properties in all directions. The isotropic character can be modified during the sintering operation at high temperatures or upon cooling to room temperature by processing techniques such as hot pressing or poling in an electric or magnetic field (see Ceramics as electrical materials).

The properties of electroceramics are related to their ceramic microstructure, ie, the grain size and shape, grain–grain orientation, and grain boundaries, as well as to the crystal structure, domain configuration, and electronic and defect structures. Electronic ceramics are often combined with metals and polymers to meet the requirements of a broad spectrum of high technology applications, computers, telecommunications, sensors (qv), and actuators. Roughly speaking, the multibillion dollar electronic ceramics market can be divided into six equal parts as shown in Figure 1. In addition to SiO_2-based optical fibers and displays, electronic ceramics encompass a wide range of materials and crystal structure families (see Table 1) used as insulators, capacitors, piezoelectrics, magnetics, semiconductor sensors, conductors, and the recently discovered high temperature superconductors. The broad scope and importance of the electronic ceramics industry is exemplified in Figure 2, which schematically displays electroceramic components utilized in the automotive industry. Currently, the growth of the electronic ceramic industry is driven by the need for large-scale integrated circuitry giving rise to new developments in materials and processes. The development of multilayer packages for the microelectronics industry, composed of multifunctional three-dimensional ceramic arrays called monolithic ceramics (MMC), continues the miniaturization process begun several decades ago to provide a new generation of robust, inexpensive products.

1. Structure-Property Relations

An overview of the atomistic and electronic phenomena utilized in electroceramic technology is given in Figure 3. More detailed discussions of compositional families and structure–property relationships can be found in other articles. (See for example, Ferroelectrics and Magnetic materials.)

Multilayer capacitors, piezoelectric transducers, and positive temperature coefficient (PTC) thermistors make use of the ferroelectric properties of barium titanate(IV) [12047-27-7], $BaTiO_3$, and lead zirconate titanate [12626-81-2]. On cooling from high temperature, these ceramics undergo phase transformations to polar structures having complex domain patterns. Large peaks in the dielectric constant accompany the phase transitions where the electric dipole moments are especially responsive to electric fields. As a result, modified compositions of barium titanate, $BaTiO_3$, are widely used in the multilayer capacitor industry and most piezoelectric transducers are made from lead zirconate titanate, $PbZr_{1-x}Ti_xO_3$, (PZT) ceramics. Applying a large

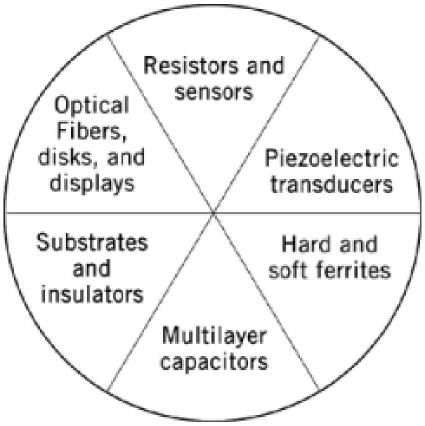

Fig. 1. Electronic ceramics market (1).

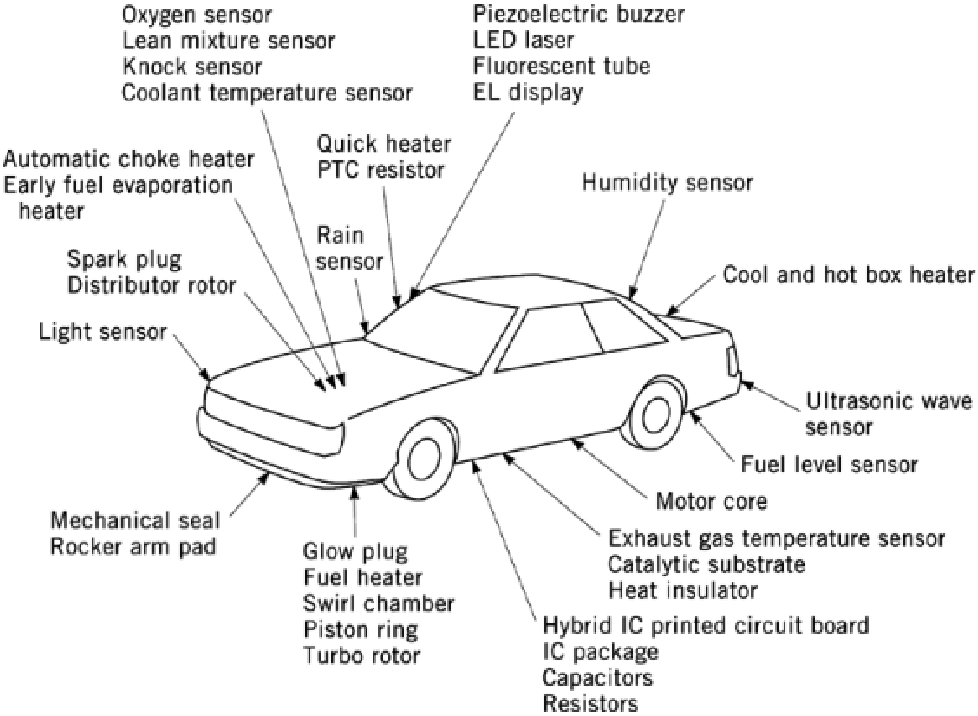

Fig. 2. Electronic ceramics for automotive applications. Courtesy of Nippon Denso, Inc.

dc field (poling) aligns the domains and makes the ceramic piezoelectric. The designation PZT is a registered trademark of Vernitron, Inc.

Similar domain phenomena are observed in ferrimagnetic oxide ceramics such as manganese ferrite [12063-10-4], $MnFe_2O_4$, and $BaFe_{11}O_{17}$, but the underlying mechanism is different. The unpaired spins of Fe^{3+} and Mn^{2+} ions give rise to magnetic dipole moments which interact via neighboring oxygen ions through a super-exchange mechanism. The magnetic dipoles are randomly oriented in the high temperature paramagnetic

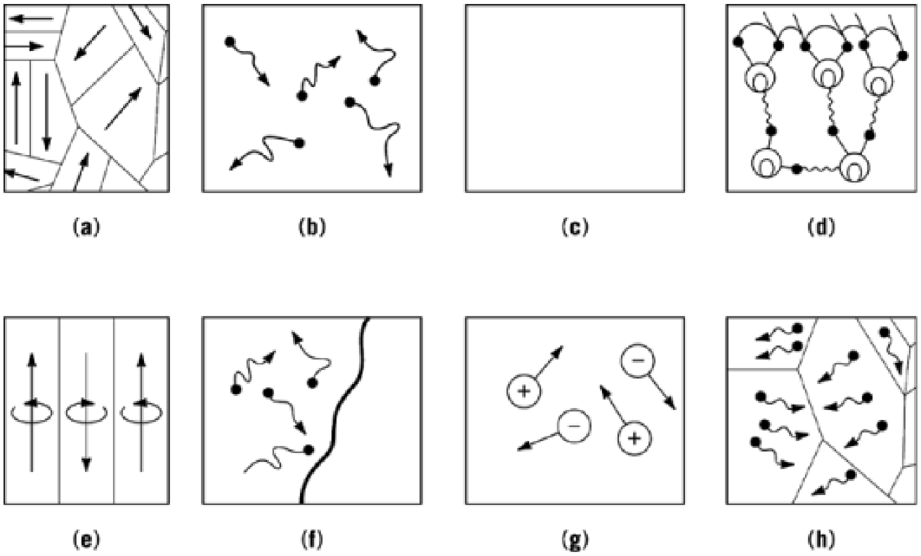

Fig. 3. An overview of atomistic mechanisms involved in electroceramic components and the corresponding uses: (**a**) ferroelectric domains: capacitors and piezoelectrics, PTC thermistors; (**b**) electronic conduction: NTC thermistor; (**c**) insulators and substrates; (**d**) surface conduction: humidity sensors; (**e**) ferrimagnetic domains: ferrite hard and soft magnets, magnetic tape; (**f**) metal—semiconductor transition: critical temperature NTC thermistor; (**g**) ionic conduction: gas sensors and batteries; and (**h**) grain boundary phenomena: varistors, boundary layer capacitors, PTC thermistors.

Table 1. Electronic Ceramic Functions and Products

Function	Material	Products[a]
insulators	porcelain, glass, steatite	high voltage insulation
packaging	Al_2O_3, BeO, AlN	IC substrates, packages (MMCs)
capacitors (energy storage)	$BaTiO_3$, $SrTiO_3$, TiO_2	multilayer and barrier layer capacitors
piezoelectrics	$Pb(Zr_{1-x}Ti_x)O_3$, SiO_2 (quartz)	vibrators, oscillators, filters, motors, and actuators
magnetics	$Mn_{1-x}Zn_xFe_2O_4$, $Ni_{1-x}Zn_xFe_2O_4$	inductors, transformers, memory devices
semiconductors	$(Ba,La)TiO_3$, V_2O_3, $Fe_{2-x}Ti_xO_3$, $ZnO–Bi_2O_3$, $MgCr_2O_4$-TiO_2, CdS, SiC	PTC, NTC-thermistors, varistors, pH sensor, humidity sensor, solar cells, electric heater
conductors	RuO_2, $NaAl_{11}O_{17}$, $Zr_{1-2x}Y_{2x}O_{2-x}$, $YBa_2Cu_3O_{7-\delta}$;	resistors (thick film), solid electrolytes, oxygen sensors, superconductors

[a] MMC = multicomponent components; PTC = positive temperature coefficient; NTC = negative temperature coefficient.

state, but on cooling through the Curie temperature, T_C, align to form magnetic domains within the ceramic grains. The peak in the magnetic permeability at T_C is analogous to the peak in the dielectric constant of ferroelectric ceramics. Domain walls move easily in soft ferrites (qv) like $MnFe_2O_4$ and γ-Fe_2O_3, which are used in transformers and magnetic tape. In barium ferrite [11138-11-7], the spins are firmly locked to the hexagonal axis, making it useful as a permanent magnet.

Several kinds of conduction mechanisms are operative in ceramic thermistors, resistors, varistors, and chemical sensors. Negative temperature coefficient (NTC) thermistors make use of the semiconducting properties of heavily doped transition metal oxides such as n-type $Fe_{2-x}Ti_xO_3$ and p-type $Ni_{1-x}Li_xO$. Thick film resistors are also made from transition-metal oxide solid solutions. Glass-bonded $Bi_{2-2x}Pb_{2x}Ru_2O_{7-x}$ having the pyrochlore [12174-36-6] structure is typical.

Phase transitions are involved in critical temperature thermistors. Vanadium, VO_2, and vanadium trioxide [1314-34-7], V_2O_3, have semiconductors–metal transitions in which the conductivity decreases by several orders of magnitude on cooling. Electronic phase transitions are also observed in superconducting ceramics like $YBa_2Cu_3O_{7-x}$, but here the conductivity increases sharply on cooling through the phase transition.

Ionic conductivity is used in oxygen sensors and in batteries (qv). Stabilized zirconia, $Zr_{1-x}Ca_xO_{2-x}$, has a very large number of oxygen vacancies and very high O^{2-} conductivity. β-Alumina [12005-48-0], $NaAl_{11}O_{17}$, is an excellent cation conductor because of the high mobility of Na^+ ions. Ceramics of β-alumina are used as the electrolyte in sodium-sulfur batteries.

Surface conduction is monitored in most humidity sensors through the use of porous ceramics of $MgCr_2O_4$–TiO_2 that adsorb water molecules which then dissociate and lower the electrical resistivity.

Grain boundary phenomena are involved in varistors, boundary layer capacitors, and PTC thermistors. The formation of thin insulating layers between conducting grains is crucial to the operation of all three components. The reversible electric breakdown in varistors has been traced to quantum mechanical tunneling through the thin insulating barriers. In a $BaTiO_3$–PTC thermistor, the electric polarization associated with the ferroelectric phase transition neutralizes the insulating barriers, causing the ceramic to lose much of its resistance below T_C. Boundary layer capacitors have somewhat thicker barriers which cannot be surmounted, and hence the ceramic remains an insulator. However, the movement of charges within the conducting ceramic grains raises the dielectric constant and increases the capacitance.

Lastly, the importance of electroceramic substrates and insulators should not be overlooked. Here one strives to raise the breakdown strength by eliminating the interesting conduction mechanisms just described. Spark plugs, high voltage insulators, and electronic substrates and packages are made from ceramics like alumina, mullite [55964-99-3], and porcelain [1332-58-7].

2. Electroceramic Processing

Fabrication technologies for all electronic ceramic materials have the same basic process steps, regardless of the application: powder preparation, powder processing, green forming, and densification.

2.1. Powder Preparation

The goal in powder preparation is to achieve a ceramic powder which yields a product satisfying specified performance standards. Examples of the most important powder preparation methods for electronic ceramics include mixing/calcination, coprecipitation from solvents, hydrothermal processing, and metal organic decomposition. The trend in powder synthesis is toward powders having particle sizes less than 1 μm and little or no hard agglomerates for enhanced reactivity and uniformity. Examples of the four basic methods are presented in Table 2 for the preparation of $BaTiO_3$ powder. Reviews of these synthesis techniques can be found in the literature (2, 5).

The mixing of components followed by calcination to the desired phase(s) and then milling is the most widely used powder preparation method (2). Mixing/calcination is straightforward, and in general, the most cost effective use of capital equipment. However, the high temperature calcination produces an agglomerated powder which requires milling. Contamination from grinding media and mill lining in the milling step can create defects in the manufactured product in the form of poorly sintered inclusions or undesirable compositional modification. Furthermore, it is difficult to achieve the desired homogeneity, stoichiometry, and phases for ceramics of complex composition.

Coprecipitation is a chemical technique in which compounds are precipitated from a precursor solution by the addition of a precipitating agent, for example, a hydroxide (5). The metal salt is then calcined to the desired phase. The advantage of this technique over mixing/calcination techniques is that more intimate mixing of the

Table 2. Methods Used to Prepare $BaTiO_3$ Electronic Ceramic Powders

Method	Reaction	Particle size
mixing/calcination[a]	$BaCO_3 + TiO_2 \xrightarrow{\Delta T} BaTiO_3 + CO_2\uparrow$	1 μm to 100s of μm
coprecipitation[b]	$Ba^{2+} + TiO^2 + 2\ C_2O_4^{2-} \xrightarrow{H_2O} BaTi(C_2O)_2{\cdot}4H_2O \xrightarrow{\Delta T} BaTiO_3 + 4\ H_2O\uparrow + 4\ CO_2\uparrow$	if calcined, mean size of $\approx$0.5 μm after milling
hydrothermal[c]	$Ba^{2+} + TiO_2 + H_2O \xrightarrow[\Delta T_1 P]{OH^-} BaTiO_3 + 2\ H_2O$	nanosize to 50 μm
metal organic decomposition[c]	$Ba(i{-}OC_3H_7)_2 + Ti(OC_4H_9)_4 + 3\ H_2O \longrightarrow BaTiO_3 + 2\ C_3H_7OH + 4\ C_4H_9OH$	5.0–35.0 nm, depending upon calcination conditions

[a] Ref. 2.
[b] Ref. 3.
[c] Ref. 4.

desired elements is easily achieved, thus allowing lower calcination temperatures. Limitations are that the calcination step may once again result in agglomeration of fine powder and the need for milling. An additional problem is that the ions used to provide the soluble salts (eg, chloride from metal chlorides) may linger in the powder after calcination, affecting the properties in the sintered material.

Hydrothermal processing uses hot (above 100°C) water under pressure to produce crystalline oxides (6). This technique has been widely used in the formation process of Al_2O_3 (Bayer Process), but not yet for other electronic powders. The situation is expected to change, however. The major advantage of the hydrothermal technique is that crystalline powders of the desired stoichiometry and phases can be prepared at temperatures significantly below those required for calcination. Another advantage is that the solution phase can be used to keep the particles separated and thus minimize agglomeration. The major limitation of hydrothermal processing is the need for the feedstocks to react in a closed system to maintain pressure and prevent boiling of the solution.

Metal organic decomposition (MOD) is a synthesis technique in which metal-containing organic chemicals react with water in a nonaqueous solvent to produce a metal hydroxide or hydrous oxide, or in special cases, an anhydrous metal oxide (7). MOD techniques can also be used to prepare nonoxide powders (8, 9). Powders may require calcination to obtain the desired phase. A major advantage of the MOD method is the control over purity and stoichiometry that can be achieved. Two limitations are atmosphere control (if required) and expense of the chemicals. However, the cost of metal organic chemicals is decreasing with greater use of MOD techniques.

2.2. Powder Processing

A basic guideline of powder manufacturing is to do as little processing as possible to achieve the targeted performance standards (see Powders, handling). Ceramic powder fabrication is an iterative process during which undesirable contaminants and defects can enter into the material at any stage. Therefore, it is best to keep the powder processing scheme as simple as possible to maintain flexibility. Uncontrollable factors such as changes in the characteristics of as-received powders must be accommodated in the processing from batch to batch of material. Keeping the processing simple is not always possible: the more complex the material system, the more complex the processing requirements.

A fundamental requirement in powder processing is characterization of the as-received powders (10–12). Many powder suppliers provide information on tap and pour densities, particle size distributions, specific surface areas, and chemical analyses. Characterization data provided by suppliers should be checked and further augmented where possible with in-house characterization. Uniaxial characterization compaction behavior, in particular, is easily measured and provides data on the nature of the agglomerates in a powder (13, 14).

Milling is required for most powders, either to reduce particle size or to aid in the mixing of component powders (15). Commonly employed types of comminution include ball milling, and vibratory, attrition, and jet

Table 3. Green Forming Procedures for Electronic Ceramics

Green forming method	Geometries	Applications
uniaxial pressing	disks, toroids, plates	disk capacitors, piezo transducers, magnets
cold isostatic pressing	complex and simple	spark plugs, ZrO_2–O_2 sensors
colloidal casting	complex shapes	crucibles, porcelain insulators
extrusion	thin sheets ($>80\ \mu m$), rods, tubes, honeycomb substrates	substrates, thermocouple insulator, catalytic converters, PTC thermistor heaters
injection molding	small complex shapes (<1.0 cm)	ZrO_2–O_2 sensors

milling, each possessing advantages and limitations for a particular application. For example, ball milling is well-suited to powder mixing but is rather inefficient for comminution.

2.3. Green Forming

Green forming is one of the most critical steps in the fabrication of electronic ceramics. The choice of green forming technique depends on the ultimate geometry required for a specific application. There are many different ways to form green ceramics, several of which are summarized in Table 3. Multilayer capacitors require preparation and stacking of two-dimensional ceramic sheets to obtain a large capacitance in a small volume. Techniques used to prepare two-dimensional sheets of green ceramic, including tape casting, (16–22) are discussed later under processing of multilayer ceramics. Manufacturing methods for ceramic capacitors have been reviewed (23).

Uniaxial pressing is the method most widely used to impart shape to ceramic powders (24). Binders, lubricants, and other additives are often incorporated into ceramic powders prior to pressing to provide strength and assist in particle compaction (25). Simple geometries such as rectangular substrates for integrated circuit (IC) packages can be made by uniaxial pressing (see Integrated circuits).

More complex shapes can be made by cold isostatic pressing (CIP). CIP uses deformable rubber molds of the required shape to contain the powder. The application of isostatic pressure to the mold suspended in a pressure transfer media, such as oil, compacts the powder. CIP is not as easily automated as uniaxial pressing, but has found wide application in the preparation of more complex shapes such as spark plug insulators (26).

Slip or colloidal casting has been used to make complex shapes in the whiteware industry for many years (24). Other work has shown that colloidal casting can be used to produce electronic ceramic materials having outstanding strength because hard agglomerates can be eliminated in the suspension processing (27–29). Colloidal casting uses a porous mold in which the fine particles in a colloidal suspension accumulate because of capillary forces at the wall surface of the mold. Relatively dense packing of the particles, to approximately 60% of theoretical density, can be achieved. More importantly, hard aggregates can be eliminated from the colloid by suitable powder selection and processing. Drying of the resulting material may not be trivial and sections greater than about ~ 1.25 cm thick are sometimes difficult to obtain.

In addition to being the preferred forming technique for ceramic rods and tubes, extrusion processes are used to fabricate the thick green sheets used in many electronic components (24, 30, 31). The smallest thickness for green sheets prepared by extrusion techniques is about 80 μm. Organic additives similar to those used in tape casting are employed to form a high viscosity plastic mass that retains its shape when extruded. The extrusion apparatus, schematically shown in Figure 4, consists of a hopper for introduction of the plasticized mass, a de-airing chamber, and either a screw-type or plunger-type transport barrel in which the pressure is generated for passage of the plastic mass through a die of the desired geometry. The plastic mass is extruded onto a carrier belt and passed through dryers to relax the plastic strain remaining after extrusion. The green sheet can be stamped or machine diced to form disks, wafers, or other platelike shapes.

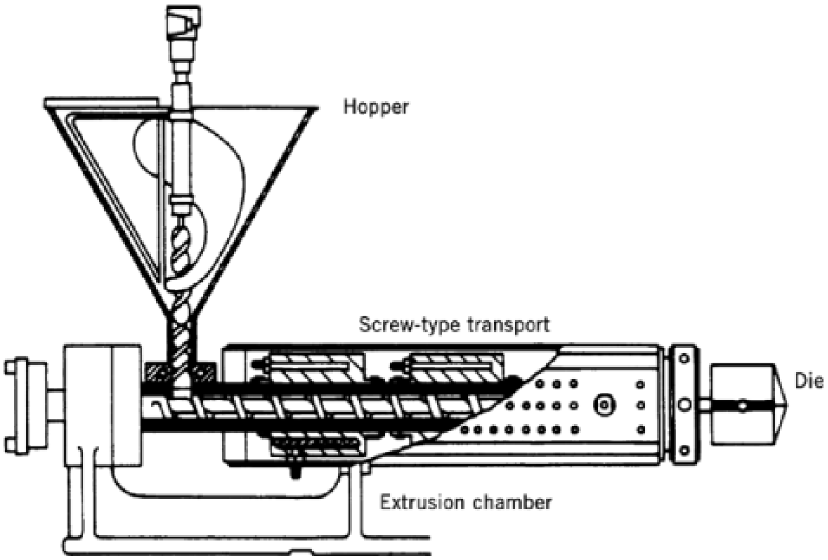

Fig. 4. Schematic of extrusion type apparatus for green sheet fabrication.

Injection molding is particularly suited to mass production of small complex shapes with relatively small (<1.0 cm) cross sections (32–34). Powders are mixed using thermoplastic polymers and other organic additives. A molten mass composed of the ceramic and a thermoplastic binder system are injected via a heated extruder into a cooled mold of desired shape. The organic is burned out and the ceramic consolidated. Machining fragments from the green ceramic can be recycled because the thermoplastic polymers can be reversibly heated. Molds can be relatively expensive so injection molding is best suited to the preparation of a large number of single parts. Because of the high organic content required, organic removal is not trivial. Green sections greater than 1.0 cm thick require slow heating rates during burnout to avoid bloating and delamination of the green ceramic.

2.4. Densification

Densification generally requires high temperatures to eliminate the porosity in green ceramics. Techniques include pressureless sintering, hot-pressing, and hot isostatic pressing (HIP). Pressureless sintering is the most widely used because of ease of operation and economics. Hot-pressing is limited to relatively simple shapes whereas more complex shapes can be consolidated using HIP (35). Sintering is used for most oxide electronic ceramics. Hot-pressing and HIP, which employ pressure and high temperatures, are used to consolidate ceramics in which dislocation motion (leading to pore elimination) is sluggish. Both techniques are particularly useful for nonoxide materials such as silicon nitride [12033-89-5] and silicon carbide [409-21-2] (35, 36) (see Carbides; Nitrides).

Special precautions are often used in the sintering of electronic ceramics. Heating rates and hold times at maximum temperature are critical to microstructural development and grain size control. Sintering cycles may include intermediate temperature annealing or controlled cooling to relieve residual strains or avoid deleterious phase transformations. Atmosphere control may be important to prevent loss of volatile components or avoid reduction reactions. In continuous production, sequential burnout (organics) and sintering may take place in the same furnace, requiring complex temperature cycles even for relatively simple devices. Complex devices

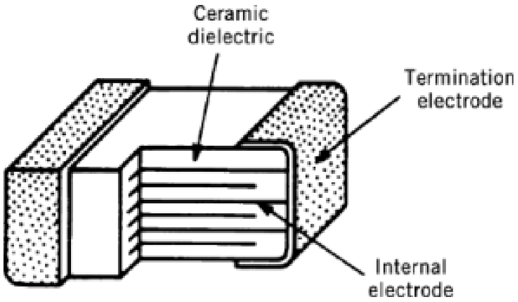

Fig. 5. Schematic cross section of a conventional MLC capacitor.

such as thick film circuits and monolithic multicomponent ceramics may require many sequential fabrication and sintering steps.

3. Processing of Multilayer Ceramics

Rapid advances in integrated circuit technology have led to improved processing and manufacturing of multilayer ceramics (MLC) especially for capacitors and microelectronic packages. The increased reliability has been the result of an enormous amount of research aimed at understanding the various microstructural–property relationships involved in the overall MLC manufacturing process. This includes powder processing, thin sheet formation, metallurgical interactions, and testing.

Presently, multilayer capacitors and packaging make up more than half the electronic ceramics market. For multilayer capacitors, more than 20 billion units are manufactured a year, outnumbering by far any other electronic ceramic component. Multilayer ceramics and hybrid packages consist of alternating layers of dielectric and metal electrodes, as shown in Figures 5 and 6, respectively. The driving force for these compact configurations is miniaturization. For capacitors, the capacitance (C) measured in units of farads, F, is

$$C = \frac{\epsilon_0 AK}{t}$$

where K is the dielectric constant (unitless); ϵ_0 the permittivity of free space = 8.85×10^{-12} F/m; A the electrode area, m^2; and t the thickness of dielectric layer, m. Thus C increases with increasing area and number of layers and decreasing thickness. Typical thicknesses range between 15 and 35 μm. Similarly, for substrate packages, the multilayer configuration incorporates transversely integrated conductor lines and vertical conducting paths (vias) allowing for numerous interconnects to components throughout the device system and power distribution in a relatively small space. MLC substrates capable of providing 12,000 electrical connections containing 350,000 vias are currently manufactured (38, 39).

A number of processing steps, shown in Figure 7, are used to obtain the multilayer configuration(s) for the ceramic-metal composites. The basic process steps are slip preparation, green tape fabrication, via-hole punching (packages), printing of internal electrodes or metallization, stacking and laminating, dicing or dimensional control, binder burnout, sintering, end termination, and encapsulation. After each processing step, quality control in the form of nondestructive physical and electrical tests ensures a uniform end-product.

The basic building block, the ceramic green sheet, starts using a mixture of dielectric powder suspended in an aqueous or nonaqueous liquid system or vehicle comprised of solvents, binders, plasticizers, and other additives to form a slip that can be cast in thin, relatively large area sheets. The purpose of the binder (20,000–30,000 molecular weight polymers) is to bind the ceramic particles together to form flexible green

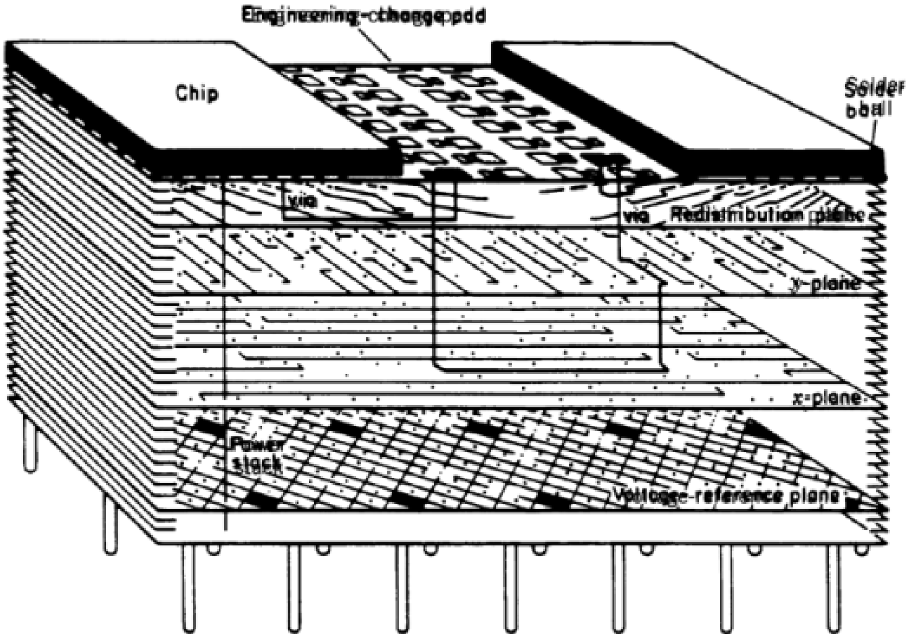

Fig. 6. Schematic of a MLC substrate for microelectronic packaging (37).

sheets. Electrodes are screened on the tape using an appropriate paste of metal powders. Solvents play a number of key roles, ranging from deagglomeration of ceramic particles to control the viscosity of the cast slip, to formation of microporosity in the sheet as the solvent evaporates. Plasticizers, ie, small to medium sized organic molecules, decrease cross-linking between binder molecules, imparting greater flexibility to the green sheet. Dispersants, typically 1,000 to 10,000 molecular weight polymer molecules, are added to slips to aid in the de-agglomeration of powder particles, allowing for higher green densities in the cast tape. Several review articles on the functional additives in tape cast systems are available (16, 17, 25, 40–44). The resulting slip should have pseudoplastic rheological behavior so that the slip flows during high shear rate casting operations, but displays little or no flow afterward, thus maintaining tape dimension (45)).

There are several methods to make large ceramic sheets for MLC manufacturing (17–23). The methods include glass, belt and carrier film casting, and wet lay down techniques. The relative advantages and limitations of each technique have been reviewed (46). The two most commonly employed techniques, belt casting and doctor blading, are depicted schematically in Figure 8.

Metallization of the green sheets is usually carried out by screen printing, whereby a suitable metal ink consisting of metal powders dispersed in resin and solvent vehicles is forced through a patterned screen. Palladium [7440-05-3] and silver–palladium (Ag:Pd) alloys are the most common form of metallization; tungsten [7440-33-7] and molybdenum [7439-98-7] are used for high ($>1500^\circ$C) temperature MLCs (47–52). Following screening, the metallized layers are stacked and laminated to register (align) and fuse the green sheets into a monolithic component. Proper registration is crucial to achieve and maintain capacitance design (MLC capacitors) and for proper via-hole placement in MLC packages.

Sintering is the most complex process in MLC fabrication. Ideally, the binder burnout and sintering steps are performed during the same temperature cycle and in the same atmosphere. Most binders burn out by 500°C, well before pore closure in the densification of most ceramics. Sintering behavior of the many different MLC components must be reconciled to achieve a dense material. Internal metallization and the dielectric

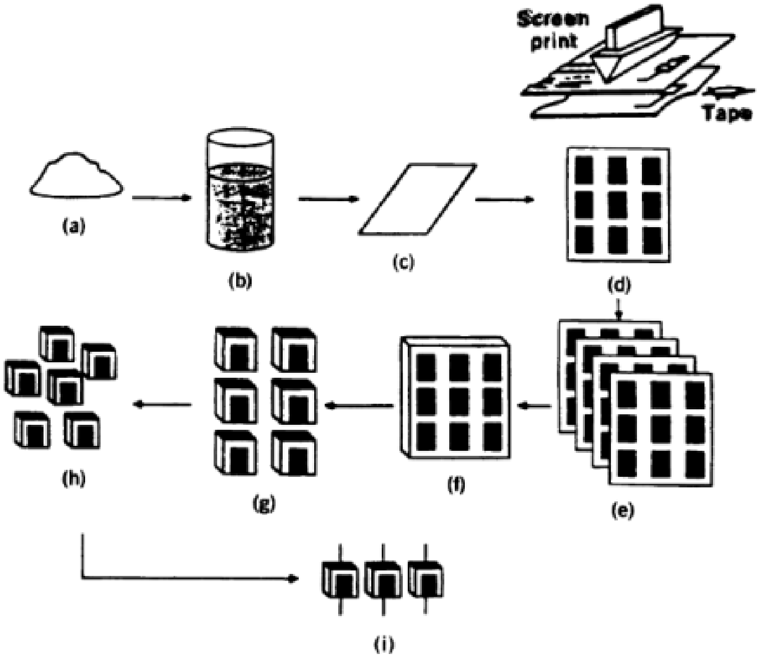

Fig. 7. Fabrication process for MLC capacitors. Steps are (**a**) powder; (**b**) slurry preparation; (**c**) tape preparation; (**d**) electroding; (**e**) stacking; (**f**) lamination; (**g**) dicing; (**h**) burnout and firing; and (**i**) termination and lead attachment.

must co-fire in a single process. Firing temperatures are related to material composition and can be adjusted using additives. Densification rates are related both to the process temperature and to particle characteristics (size, size distribution, and state of agglomeration). Thus, the burnout and sintering conditions depend heavily on the system.

After densification, external electrode termination and leads are attached for MLC capacitor components, and pin module assembly and IC chip joining is carried out for MLC packages. The devices are then tested to ensure performance and overall reliability.

4. Thick Film Technology

Equally important as tape casting in the fabrication of multilayer ceramics is thick film processing. Thick film technology is widely used in microelectronics for resistor networks, hybrid integrated circuitry, and discrete components, such as capacitors and inductors along with metallization of MLC capacitors and packages as mentioned above.

In principle, the process is equivalent to the silk-screening technique whereby the printable components, paste or inks, are forced through a screen with a rubber or plastic squeegee (see Fig. 7). Generally, stainless steel or nylon filament screens are masked using a polymeric material forming the desired printed pattern in which the composition is forced through to the underlying substrate.

Thick film compositions possess three parts: (*1*) functional phase, (*2*) binder, and (*3*) vehicle. The functional phase includes various metal powders for conductors, electronic ceramics for resistors, and dielectrics for both capacitors and insulation. Examples of typical components for thick film compositions are given in Table 4 The binder phase, usually a low ($<1000^\circ C$) melting glass adheres the fired film to the substrate whereas

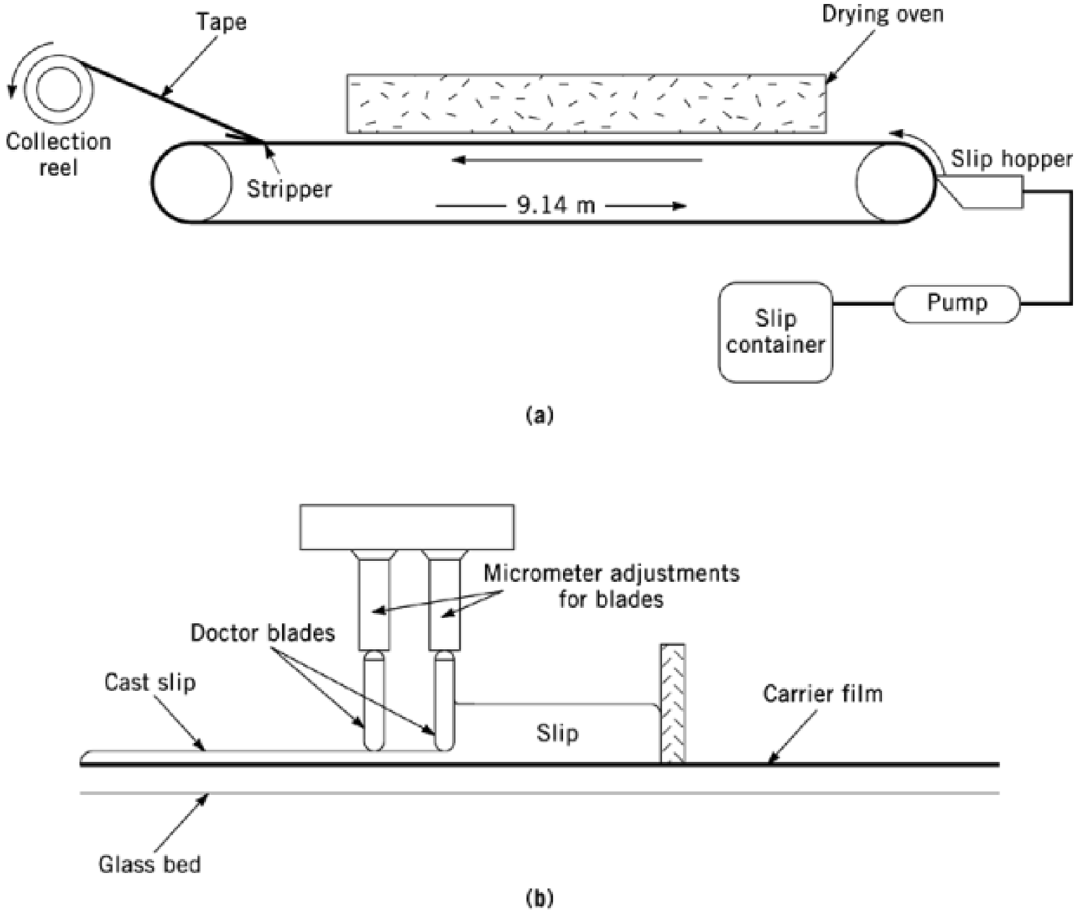

Fig. 8. Schematic of methods for MLC manufacturing; (**a**) belt casting; (**b**) carrier film casting using a doctor blade.

the fluid vehicle serves to temporarily hold the unfired film together and provide proper rheological behavior during screen printing. Thick film processing for hybrid integrated circuits typically takes place below 1000°C providing flexible circuit designs.

5. Current and Future Developments in Multilayer Electronic Ceramics

Advances in the field of electronic ceramics are being made in new materials, novel powder synthesis methods, and in ceramic integration. Monolithic multicomponent components (MMC) take advantage of three existing technologies: (*1*) thick film methods and materials, (*2*) MLC capacitor processes, and (*3*) the concept of cofired packages as presented in Figure 9. Figure 10 shows an exploded view of a monolithic multicomponent ceramic substrate.

New materials for packaging include aluminum nitride [24304-00-5], AlN, silicon carbide [409-21-2], SiC, and low thermal expansion glass-ceramics, replacing present day alumina packaging technology. As shown in Table 5, these new materials offer significant advantages to meeting the future requirements of the microelectronics industry. Properties include higher thermal conductivity, lower dielectric constant, cofire

Table 4. Components of Thick Film Compositions[a]

Component	Composition
functional phase	
conductor	Au, Pt/Au
	Ag, Pd/Ag
	Cu, Ni
resistor	RuO_2
	$Bi_2Ru_2O_7$
	LaB_6
dielectric	$BaTiO_3$
	glass
	glass–ceramic
	Al_2O_3
binder	glass: borosilicates, aluminosilicates
	oxides: CuO, CdO
vehicle	volatile phase: terpineol, mineral spirits
	nonvolatiles: ethyl cellulose, acrylates

[a] Ref. 53

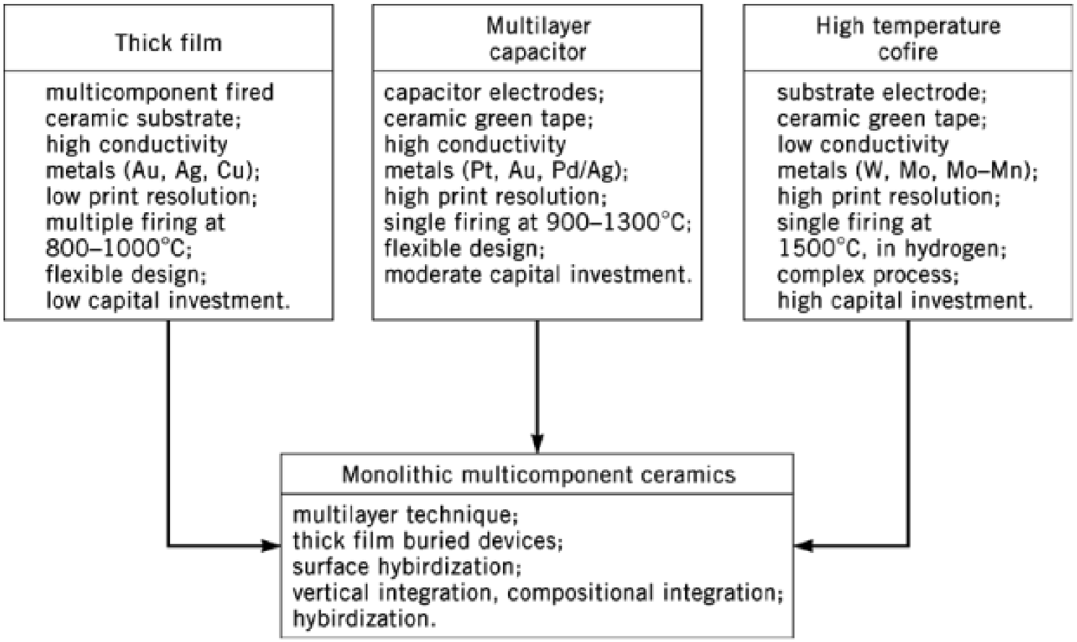

Fig. 9. Monolithic multilayer ceramics (MMCs) derived from multilayer capacitor, high temperature cofire, and thick film technologies.

compatibility, and related packaging characteristics such as thermal expansion matching of silicon and high mechanical strength as compared to Al_2O_3.

Greater dimensional control and thinner tapes in multilayer ceramics are the driving forces for techniques to prepare finer particles. Metal organic decomposition and hydrothermal processing are two synthesis methods that have the potential to produce submicrometer powders having low levels of agglomeration to meet the demand for more precise tape fabrication.

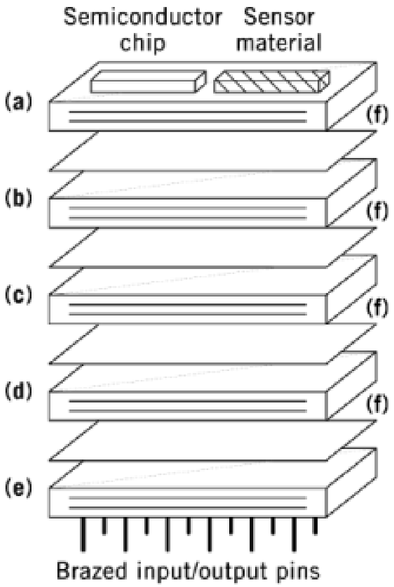

Fig. 10. Exploded view of a monolithic multicomponent ceramic substrate. Layers (**a**) signal distribution; (**b**) resistor; (**c**) capacitor; (**d**) circuit protection; and (**e**) power distribution are separated by (**f**) barrier layers.

Table 5. Properties of High Performance Ceramic Substrates[a]

Properties	AlN	SiC	Glass-ceramics	90% Al_2O_3
thermal conductivity, W/(m·K)	230	270	5	20
thermal expansion coefficient, RT – 400°C × 10^{-7}/°C[b]	43	37	30–42	67
dielectric constant at 1 MHz	8.9	42	3.9–7.8	9.4
flexural strength, kg/cm^2	3500–4000	4500	1500	3000
thin film metals	Ti/Pd/Au Ni/Cr/Pd/Au	Ti/Cu	Cr/Cu, Au	Cr/Cu
thick film metals	Ag–Pd Cu	Au Ag–Pd	Au, Cu, Ag–Pd	Ag–Pd Cu, Au
cofired metals	W	Mo	Au–Cu, Ag–Pd	W, Mo
cooling capability, °C/W				
air	6	5	60	30
water[c]	<1	<1	<1	<1

[a] Ref. 39.
[b] RT = room temperature.
[c] External cooling.

As stated above, the development of multifunctional MLCs based on existing technologies offers excellent growth potential since MMCs combine the possibilities of both the high cofire (packaged) substrates and burial of surface devices (54–57). Burial of surface devices promises gains in both circuit density and device hermiticity, leading to increased reliability. Processing trade-offs are expected since current electronic materials for multilayer applications (capacitors, transducers, sensors) are densified at very different firing temperatures. Consequently, integrated components will likely be of lower tolerance and limited range, at least in the early developmental stages. Current efforts have been directed toward incorporation of multilayer capacitor-type power planes and burial of thick film components, including resistors and capacitors. The latter processing

Table 6. Current and Future Developments in Thin Film Electronic Ceramics[a]

Material	Application	Methods
PT, PZT, PLZT	nonvolatile memory, ir, pyroelectric detectors, electro–optic waveguide, and spatial light modulators	sol–gel, sputtering
diamond (C)	cutting tools, high temperature semiconductors, protective optical coatings	chemical vapor deposition (CVD)
SiO_2, $BaTiO_3$	capacitors	sol–gel, sputtering, chemical vapor deposition (CVD)
1:2:3 superconductors	squids, nmr, interconnects	

[a] Refs. 58 and 59.

technology offers more immediate possibilities as it is developed to cofire at conventional thick film processing temperatures for which a wide range of materials exist.

The continuing miniaturization of electronic packaging should see the replacement of components and processes using such thin film technologies developed for semiconductors as sputtering, chemical vapor deposition, and sol–gel (see Sol–gel technology; Thin films) (58, 59). Sputtering is the process whereby a target material is bombarded by high energy ions which liberate atomic species from the target for deposition on a substrate. Chemical vapor deposition (CVD) involves a gaseous stream of precursors containing the reactive constituents for the desired thin film material, generally reacted on a heated substrate. The more recent process for thin films, sol–gel, uses a nonaqueous solution of metal—organic precursor. Through controlled hydrolyses, a thin, adherent film is prepared by dip-coating or spin-coating. The dried “gel” film is then crystallized and densified through heat treatments. Both existing and future developments of thin film electronic ceramics and methods are presented in Table 6.

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