

## Advanced ceramics – an overview

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**Abstract.** In sharp contrast to conventional ceramics, advanced ceramics use extensively processed starting materials of controlled purity and particle size, and novel fabrication techniques such as tape casting, chemical vapour deposition, *in situ* oxidation, injection moulding, followed by fast, often low temperature, sintering. Advanced ceramics exhibit unusual behaviour at times and quantum jumps in properties. Improved fracture toughness of structural ceramics makes them suitable candidates for stringent engineering applications. Composites involving special ceramics display some outstanding properties, e.g. piezoelectrics. Examples of dielectrics, super conductors, optical fibres and ionic conductors are cited.

**Keywords.** Materials preparation; processing; superconductors; optical fibres; toughened ceramics; composites.

### 1. Introduction

From the beginning of civilisation, ceramics provided objects of utility and beauty. Shelter for mankind is based on adobe, brick, tile, cement and window glass. Cooking and storing of food has always been done in ceramicware ranging from clay pots to modern glass-ceramics. The abundant and widespread availability of basic ceramic raw materials—clay, sand and other minerals—in nature enabled ceramics to meet basic human needs over the millennia. The growth in world population guaranteed the expansion of the traditional ceramic industry.

Superimposed on this steady, but slow, growth of ceramics, has been an important qualitative change in recent decades, based on a deeper scientific understanding of the composition-structure-processing-property correlations of ceramics. This arose in response to the stringent requirements of sophisticated applications in electronics, space, nucleonics and energy, among others. Ceramics to meet these newer, engineering applications are termed advanced ceramics (Subbarao 1987). Together with biotechnology and electronics, advanced ceramics has moved to the centre-stage of the second industrial revolution to propel mankind into the twenty-first century. The characteristics of these new-born industries are manifold increases in properties and performance, as well as typical annual growth rates of 50–100% (Kenney & Bowen 1983).

In this exciting area, a few pockets of excellence exist in India, which have made respectable contributions to the worldwide progress in advanced ceramics.

In this paper, the distinction between advanced and conventional ceramics is outlined, followed by an overview of the new material preparation techniques, their unusual processing methods, and the quantum jumps observed in their properties for meeting the stringent requirements of emerging engineering applications.

## 2. Characteristics

The important differences between conventional and advanced ceramics are summarised in table 1.

Modern applications call for enhanced, reliable properties, which can be met only when the starting materials have reproducible characteristics. This is not possible with naturally occurring minerals and ores, even after beneficiation. The higher cost of processed materials has to be justified by enhanced performance. Empiricism and experience which guided conventional ceramics are totally inadequate, and often inappropriate, for advanced ceramics, which can progress only through knowledge gained by multidisciplinary research and development.

## 3. Material preparation

The materials for advanced ceramics must possess:

- (i) high purity—may be as high as 99.99%;
- (ii) small and uniform particle size, which gives rise to large surface area and high reactivity;
- (iii) reproducibility—homogeneous distribution of intentionally added impurities, called dopants, which may be present at ppm level.

Novel preparation techniques, such as sol-gel (Roy & Roy 1984; Lannutti & Clark 1985; Sen & Chakravorty 1986), precursors (Rao 1986; Mazdidasni 1982), alkoxides (Mazdidasni 1982), and topochemistry (Gopalakrishnan 1986), for this purpose arose from developments in solid state chemistry. These methods have made it possible to

**Table 1.** Distinctions between conventional and advanced ceramics.

Characteristic	Conventional	Advanced
Raw materials	Natural minerals with little or no processing e.g. clay, sand	Processed materials e.g. $Al_2O_3$ , $ZrO_2$ , $Si_3N_4$ , SiC, SiAlON
Processing	Pressing, extrusion, slip casting, drying, firing	Tape casting, hot isostatic pressing, injection moulding, CVD, <i>in situ</i> oxidation
Properties	Refractoriness, thermal & electrical insulation	Fracture toughness, electrical conductivity, electro-optics, dielectrics, piezoelectrics, magnetics, superconductivity
Applications	Refractories, sanitary-ware, sheet glass, building materials	Diesel engine, optical fibre, substrate, ferrites, capacitors, transducers

produce some materials which could not be produced otherwise. For example, utilising solid solution precursors of  $\text{Ca}_{1-x}\text{Mn}_x\text{CO}_3$ , a variety of oxides in the Ca-Mn-O system have been synthesised (Vidyasagar *et al* 1985). Some of the mixed carbonates which occur in nature could be made in the laboratory only by the precursor method. Similarly, dehydration as well as insertion and removal of protons, lithium ions etc. into compounds in a reversible way can be accomplished through topochemical reactions. Hydrolysis of zirconium tetrabutoxide in alcohol solution can be used to produce monodispersed  $\text{ZrO}_2$  powders (Ogihara *et al* 1987).

Chemically prepared zirconia can be sintered to high density at  $1400^\circ\text{C}$ , several hundred degrees less than the usual temperatures (Gupta *et al* 1977). The incorporation of small quantities of La in  $\text{BaTiO}_3$  to decrease its electrical resistivity by a factor of  $10^{10}$  is best accomplished by a solution-decomposition route. These new methods enable mixing at an atomic scale, compared to the gross particle mixing by mechanical means, employed in conventional ceramic processing. The atomic level mixing means shorter diffusion distances for material transport (about  $10 \text{ \AA}$  compared to about  $10,000 \text{ \AA}$  in mixing of ceramic powders), leading to decreased temperatures and duration for sintering, besides greater compositional homogeneity. The disordered atomic arrangement in a gel is a better starting point for making glasses, which are amorphous in nature, compared to the use of well-crystallised oxides and other salts (Chakravorty 1988).

Alumina is by far the most important base material for advanced ceramics and accounts for over 80% of the raw materials employed in engineering ceramics. The other materials of importance are  $\text{BaTiO}_3$ ,  $\text{TiO}_2$ , lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT),  $\text{ZrO}_2$ , SiC,  $\text{Si}_3\text{N}_4$  and SiAlON.

#### 4. Processing

While all the conventional ceramic processes such as pressing, slip casting, extrusion, drying, firing etc., are available for advanced ceramics, some newer fabrication technologies are developed to meet specific requirements. These include:

- (i) Isostatic and hot isostatic pressing to achieve higher end point density and freedom from defects such as laminations, density gradients etc.
- (ii) Tape casting to produce thin sheets of large area from a slurry of alumina, titanates etc., spread by a blade on a moving plastic sheet (Williams 1976; Prasad 1988). The surface of such substrates has a high degree of evenness (typically a few microns per linear meter). These sheets are often stacked in the green condition, with metal electrode paste applied over the entire area or as thin lines, and then the stack is fired to produce multilayer capacitors. Alumina sheets with a network of resistor and conductor paste, in the form of thin lines, are stacked (upto 150 layers) and fired to produce multilayer ceramic chips for modern computers. The manufacture of multilayer ceramics including metallic interconnections is often completed in a single firing operation (Dougherty & Greer 1983).
- (iii) Injection moulding for small intricate shapes with projections and perforations.
- (iv) Chemical vapour deposition of preforms from which optical fibres are drawn (MacChesney 1981, pp. 537–561).
- (v) *In situ* oxidation. A component is cast from molten aluminium alloy and oxidation is allowed to take place at the moving liquid/solid interface to result in an

alumina component of the desired shape. The multitude of steps normally employed in the fabrication of alumina components is replaced by a single casting-oxidation step, which is completed at a much lower temperature and shorter time than those employed for sintering of alumina ceramics.

(vi) Electrophoretic deposition of beta-alumina electrode tubes for Na-S battery (Krishnarao *et al* 1986).

(vii) Sintering at a lower temperature and in shorter time. Ceramic dielectrics are now fired at temperatures below 1000°C compared to the usual 1300–1350°C employed for sintering titanate dielectrics. The entire sintering operation is completed in 1–2 h, much shorter than the traditional 20–24 h. The resulting energy saving is substantial. These improvements in sintering are due to:

- (a) increased sinterability of the highly reactive, small particle size initial powders;
- (b) sintering aids which provide transient liquid phase (Ramesh Choudhary & Subbarao 1981; Prasad 1988); and
- (c) lower melting compositions such as niobates in place of titanates (Prasad 1988).

Since advanced ceramics are often used in engineering applications, often as components in a larger assembly, their dimensional tolerance, integrity and reproducibility are considerably more critical than those of conventional ceramics. Finishing operations, such as grinding, polishing etc., are expensive and may introduce defects and therefore should be employed sparingly. Hence, processing methods preferred for advanced ceramics are those which give the final net shape within required dimensional tolerance, with little or no subsequent finishing operations.

The high cost of starting materials, stringent specifications on properties and dimensions, and the need for reproducibility usually dictate the automation of the fabrication steps. The controls inherent in automation require a deeper knowledge of composition-structure-processing-property interdependence. The recent advances in ceramic science are making this possible.

## 5. Properties

The properties of advanced ceramics are both quantitatively and, more importantly, qualitatively different from those of conventional ceramics. Following the successive replacement of vacuum tubes by transistors, integrated circuits and large scale integrated circuits (LSI), miniaturisation of other circuit elements such as ceramic capacitors has become necessary. This is achieved by gradual increase in the dielectric constant of capacitor materials by almost an order of magnitude every decade (figure 1). While  $\text{TiO}_2$  and  $\text{BaTiO}_3$  are new classes of dielectric materials, improvements in the last 30 years are due to modification of the basic titanate material. These innovations include fine grain size to inhibit domain reorientations (Buessem *et al* 1966), stacking of thin layers in a multilayer capacitor (Prasad 1988) or development of an insulating layer surrounding semiconducting titanate grain (Goodman 1981; Wernicke 1981).

While barium titanate is valued for its high electrical resistivity ( $> 10^{10}$  ohm cm) when it is used as a capacitor, it can be made semiconducting (resistivity  $\approx 10^2$  ohm cm) by doping it with a small amount of La or many other ions (analogous to semi-

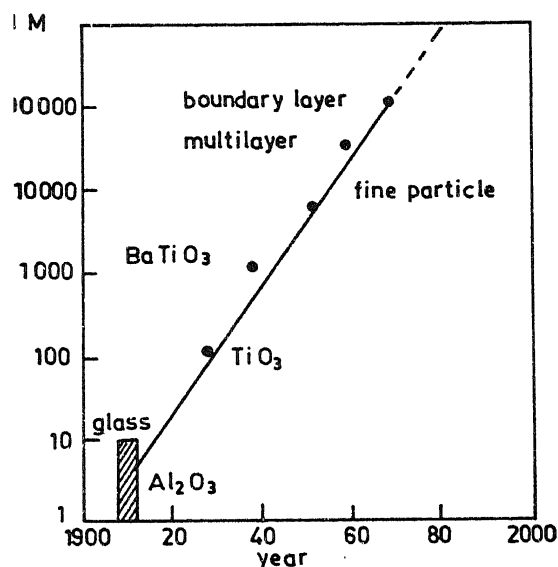


Figure 1. Chronology of enhancement of dielectric constants of ceramic dielectrics.

ductor technology). The electrical resistivity of such a semiconducting barium titanate increases sharply (by about  $10^4$ ) in the vicinity of its ferroelectric Curie temperature (Kulwicki 1981). This positive temperature coefficient of resistivity (PTCR) is made use of for motor protection, self-regulating heaters, etc.

Zirconia, doped with CaO, MgO, Y<sub>2</sub>O<sub>3</sub> etc., exhibits a cubic, fluorite type structure. It has been established that the dopant cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Y<sup>3+</sup> etc.) replace the Zr<sup>4+</sup> ions and the charge balance is restored by the creation of an appropriate number of oxygen ion vacancies (Subbarao 1980). The existence of the oxygen ion vacancies, whose concentration is fixed by the amount of dopant and remains independent of temperature and oxygen partial pressure, leads to oxygen ion diffusion at rates a million-fold higher than that of cations (Subbarao 1981). Accompanying the mass transport of oxygen ions through the cubic zirconia lattice, there is charge transport according to the Nernst–Einstein relationship

$$E = (RT/4F) \ln [P_{O_2}/P_{O_2(\text{ref})}] \quad (1)$$

where  $E$  is the EMF set up when a zirconia membrane separates gases with oxygen partial pressures of  $P_{O_2}$  and  $P_{O_2}$  (reference, say air),  $R$  is the gas constant,  $T$  is absolute temperature and  $F$  is the Faraday constant. Zirconia oxygen probes, using a variation of a potential, dictated by (1), to a zirconia membrane can pump oxygen to or out of a gas stream to attain a desired oxygen content (down to a few parts per billion) (Subbarao & Maiti 1987). When the oxygen required for combustion in a fuel cell is transported across a zirconia membrane, the EMF developed becomes available to perform useful work. Such a zirconia-based high temperature fuel cell is an efficient power source without any moving parts (Maiti & Paria 1988).

In a beta-alumina lattice, Na<sup>+</sup> ions occupy some of the interstices between the thin alumina blocks. The fact that only a few of the available sites are occupied by the Na<sup>+</sup> ions and the inter-ionic distances are larger than the size of the Na<sup>+</sup> ion enables easy sodium ion diffusion, making beta-alumina a suitable solid electrolyte separating two molten electrodes—sodium and sulphur—in a high energy density

battery, called the sodium-sulphur battery (Subbarao 1980). Since these batteries have a much higher energy density per unit weight or volume, compared to the conventional lead-acid battery, they are good candidates for load levelling and, possibly, automotive applications.

Since superconductivity was discovered in 1911 in solid mercury by Kammerlingh Onnes, only a few metals have exhibited this unique property. The transition from the normal to the superconducting state (which is signalled by a near total loss of electrical resistivity) arises a few degrees above absolute zero (less than 10 K) in these metals (table 2). After a gap of nearly 40 years during which the superconducting transition temperature nearly stagnated, a number of intermetallics in which the superconducting transition temperature was in the range of 10–20° K were found. Nb<sub>3</sub>Ge exhibiting a record  $T_c$  of 23 K (table 2) was discovered in 1973. After a gap of 13 years, Bednorz & Müller (1986) found that a rare earth–Ba–Cu oxide exhibits superconductivity at 36 K. This outstanding discovery started an intense scientific effort all over the world and a  $T_c$  of 100 K, above the liquid nitrogen temperature (77 K), was achieved in a matter of weeks for a number of oxides. Originally thought of as La<sub>2-x</sub>M<sub>x</sub>CuO<sub>4</sub> where M = Ba, Sr, the superconducting oxide was reported as Y<sub>1.2</sub>Ba<sub>0.8</sub>CuO<sub>4</sub> (Wu *et al* 1987) with K<sub>2</sub>NiF<sub>4</sub> structure type. Ganguly *et al* (1987a) reported a  $T_c$  of 100–120 K for oxides in the system Y–Ba–Cu–O. The compound YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7±δ</sub> was found to have a perovskite-type (and not K<sub>2</sub>NiF<sub>4</sub> type) structure (Ganguly *et al* 1987b). Other reports in this field, all in a space of three months, are by Uchida *et al* (1987), Chu *et al* (1987), Cava *et al* (1987) and Rao & Ganguly (1987). It may be noted from table 2 and figure 2 that metals exhibit superconducting transition temperatures ( $T_c$ ) under 10 K, intermetallic compounds have  $T_c$  upto 23 K and oxides, discovered in 1986–87, have  $T_c$  between 36 and 120 K. There are claims of oxides with  $T_c$  of 240 K, not much below the temperature of an ordinary refrigerator, if not of a room. The critical current density of these superconducting oxides is steadily increasing, so that device research has already begun. Superconductors are often used in the form of wires, made into coils, for producing intense magnetic fields. The production of flexible, long shapes from the conven-

Table 2. Superconducting materials and critical temperatures.

Metals	$T_c$ (K)	Intermetallics	$T_c$ (K)	Oxides	$T_c$ (K)
Ti	0.53	Pb <sub>2</sub> Au	7.0	La <sub>2-x</sub> M <sub>x</sub> CuO <sub>4</sub>	≥ 36
Zr	0.7	SnSb	3.9	M = Ba, Sr	
Hf	0.35	Tl <sub>3</sub> Bi <sub>5</sub>	6.4	Y <sub>1.2</sub> Ba <sub>0.8</sub> CuO <sub>4</sub>	
Th	1.32	WC	2.5–4.2	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7±δ</sub>	~ 100
V	5.1	MoC	7.6–8.3	Bi–Sr–Ca–Cu–O	~ 105
Nb	9.22	MoN	12.0	Tl–Ba–Ca–Cu–O	85–130
Ta	4.38	NbN	14.7		
Zn	0.79	Nb <sub>3</sub> Sn	18.07		
Cd	0.54	Nb <sub>3</sub> Al	18		
Hg	4.12	V <sub>3</sub> Si	16.8–17.1		
Al	1.14	V <sub>3</sub> Ga	16.8		
Ga	1.07	Nb–25% Zr	10.8		
In	3.37	Nb–60% Ti	8.7		
Tl	2.38	Nb–Al–Ge	20		
Sn	3.69	Nb <sub>3</sub> Ge	23.2		
Pb	7.26				

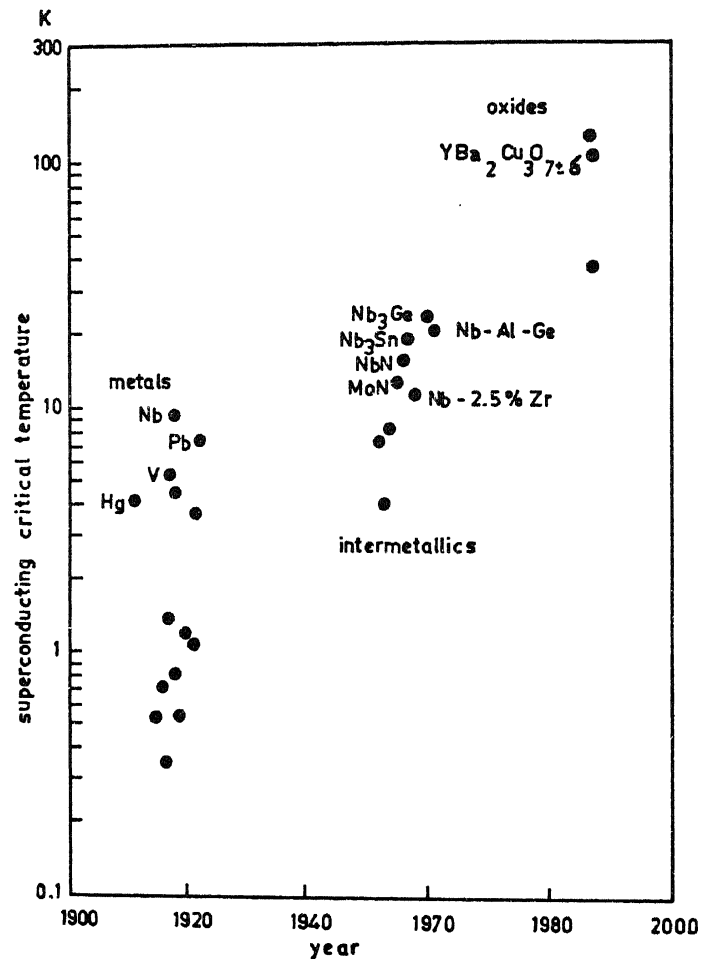


Figure 2. Remarkable trend of critical temperatures of superconducting metals, intermetallics and oxides.

tionally brittle ceramics is a challenging task. Novel fabrication techniques are being conceived, besides the established thin film methods.

This discovery of superconducting ceramics, when it is translated into commercial technology, is likely to have a major impact on electrical engineering practice including power transmission, energy storage, computer size, levitated transport (train and ship), nuclear fusion, medical diagnostics etc. (Rao 1988a).

Glass fibres have been used for decades for reinforcing plastics, as well as for thermal and sound insulation. The current interest in silica glass fibre stems from the discovery of its ability to transmit electrical signals over long distances with little attenuation (MacChesney 1981, pp. 537–561). Transmission losses are attributed to the presence of transition metal ions in starting materials which can be reduced through purification. For example, a single glass fibre can send  $2 \times 10^{10}$  bits of information per second over a distance of 68 km length of fibre. This is equivalent to sending the data in 200 encyclopaedia volumes per second. The distance between repeaters in presently installed fibres is 30 km, which is expected to increase to

300 km. The repeaters, located between the light source and detectors in an optical fibre system, control the shape, time and strength of the weakening optical signals. The additional advantages of optical glass fibre over the conventional copper wire for transmission of information are its light weight, the abundance of raw materials, its lower cost, environmental stability, and insensitivity to electromagnetic interference. The material preparation and fibre production technologies, as well as the clean environment of the production facilities, are more akin to the semiconductor industry than to a ceramic factory. More recently, fluoride glasses ( $\text{ZrF}_4\text{-ThF}_4\text{-BeF}_2$ ) have shown lower transmission losses (0.01 to 0.001 dB/km) compared to about 0.2 dB/km for silica optical fibres. The decreasing trend of losses of transmission fibres is shown in figure 3 (Tummala & Shaw 1987). It shows that they have decreased from 10–200 dB/km for multicomponent glasses 20 years ago to 2–4 dB/km for present commercial silica fibres, and to 0.1 dB/km for laboratory fibres.

While ceramics are quite strong under compression, they are generally weak in tension and are rarely free from flaws which lead to brittle fracture, often catastrophically. This deficiency has been overcome in the case of glass by placing the surface under compression, either through a heat treatment operation, called tempering, or through ion exchange from molten salts. In crystalline ceramics, the presence of cracks and other flaws cannot be completely avoided. Therefore, recourse is taken to methods for inhibiting crack growth. One way to do so is by the incorporation of fibres. Another way is to utilise a phase transformation to absorb

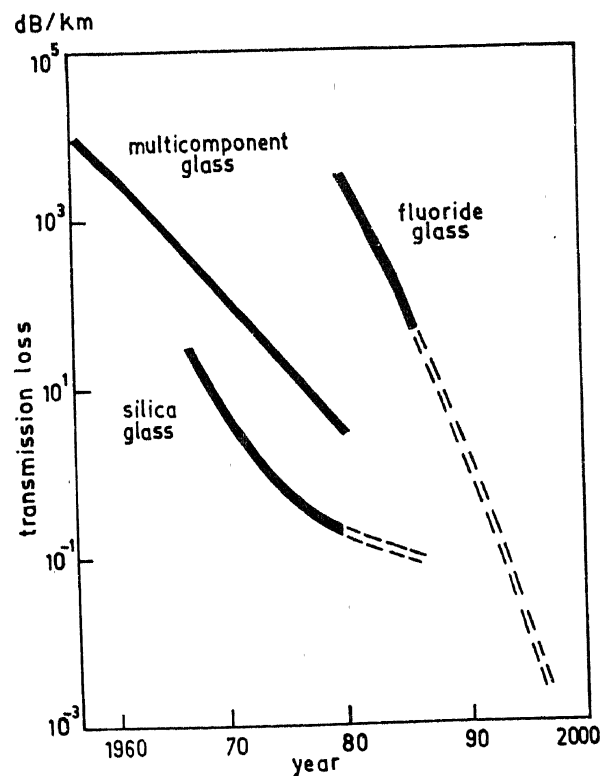


Figure 3. Trend of transmission losses of optical fibres.



the energy associated with a stress concentration. In fact, both can be combined as was done by Claussen (1986) in the case of fibre-reinforced transformation-toughened zirconia. While fibre-reinforcement as a strengthening mechanism has been practised for quite sometime, strengthening and toughening of ceramics via a phase transformation was first demonstrated in zirconia by Garvie *et al* (1975). Here the volume change accompanying the martensitic phase transition of zirconia (tetragonal to monoclinic) is exploited. The underlying mechanisms are reviewed by Bhaduri (1988). The transformation-toughened zirconia ceramics are used as dies for hot extrusion of ferrous and non-ferrous metals, engine and pump components, textile thread guides etc.

Silicon carbide, silicon nitride ( $\text{Si}_3\text{N}_4$ ) and its derivative SiAlON are excellent structural ceramics, as discussed by Rao (1988b), and are good machining tool bits (Komanduri 1988).

Only a third of the fuel energy is utilised in the shaft power of an internal combustion or a diesel engine, with one-third wasted in the coolant and another third escaping with the exhaust (Horton & Compton 1984). Since metal components limit the temperature of operation of the engine, necessitating efficient cooling, advanced ceramic components are under examination for various parts of the engine. Significant improvement in engine efficiency is achieved because of the higher temperature at which the engine with ceramic components (as coatings, liners, or as such) can be operated, with consequent higher Carnot efficiency, and requiring less cooling. The higher operating temperatures also have a favourable effect on engine emissions. The ceramic coating technology is reviewed by Karthikeyan & Mayuram (1988).

One more point needs to be emphasized regarding structural ceramics. In order to achieve optimal benefit from structural ceramics, one should, instead of making a simple replacement of a metal part by a ceramic item, redesign the part taking into account the unique properties, including brittle fracture, of ceramics.

Only the unique, new or enhanced properties of advanced ceramics are discussed here. It must however be emphasized that all the other properties which have made conventional ceramics such useful materials are also exhibited by advanced ceramics. These include extreme inertness to environment and temperature, lightness, abundance of raw materials, a range of thermal expansion and thermal conductivity etc. If conventional ceramics responded to the basic needs of man, advanced ceramics answer the challenges posed by sophisticated industries.

## 6. Composites

A single-phase material with many excellent properties may still suffer from some deficiencies. This can be overcome by combining the desirable properties of two materials in the form of a composite. Fibre-reinforced materials, such as bamboo in adobe, steel rods in concrete, glass fibres in plastics, are well-established structural materials. Porous insulating materials are composites of solid and gas phases. Most ceramic products are composed of crystalline and glassy phases. Bone is a unique composite of a crystalline phosphate and a pore phase, with three dimensional connectivity for both phases. This has formed the basis for the development of

biocompatible ceramics, glasses and glass-ceramics for biomedical applications and as implants.

The chronological improvements in properties and the role of composites may be illustrated by the development of piezoelectric materials. In early 1940's the ferroelectric behaviour of barium titanate was discovered. Since a ferroelectric is, by definition, a piezoelectric, barium titanate became an important piezoelectric material. In the late 1940's, when it was demonstrated that ceramic barium titanate can be poled to confer non-isotropic domain orientation, ceramic barium titanate became the first piezoelectric, which is not a single crystal (unlike quartz, Rochelle's salt, potassium dihydrogen phosphate etc.), and has all the unique properties of a ceramic—stability, ease of fabrication etc. Further, the piezoelectric properties of barium titanate were much higher than those of the single crystal piezoelectrics e.g. quartz. Soon after the discovery of ferroelectricity in  $\text{BaTiO}_3$ , a variety of ionic substitutions (for Ba and Ti) were attempted which resulted in a number of new ferroelectrics, such as  $\text{PbTiO}_3$ , which is isostructural (perovskite-type) with  $\text{BaTiO}_3$ . In 1950,  $\text{PbZrO}_3$  was found to be isostructural with  $\text{BaTiO}_3$  and also to possess spontaneous polarization. However, each crystallographic plane in it has its spontaneous polarization aligned in one direction but neighbouring planes have their polarization in opposite directions. Spontaneously polarized materials with antiparallel orientation of polarization in adjacent planes, leading to net zero polarization, are termed antiferroelectrics, in analogy with antiferromagnets.  $\text{PbZrO}_3$ , thus, became the first antiferroelectric. A study of the perovskite compositions in the binary system  $\text{PbTiO}_3$ - $\text{PbZrO}_3$  revealed a morphotropic phase boundary near the equimolar composition, which exhibits greatly enhanced piezoelectric modulus (Jona & Shirane 1962). Efforts over the next quarter century have not produced any piezoelectric material better than lead zirconate titanate (PZT). Newnham *et al* (1980) have produced PZT-polymer composites which have piezoelectric properties one to two orders of magnitude better than PZT itself. These composites contain only 10% of PZT mixed with 90% of inexpensive polymer. The size and distribution of the two phases are important parameters, but equally crucial is the connectivity of each phase. By assigning values of 0 (for unconnected), 1 (for rods), 2 (for sheets) and 3 (for three-dimensional continuity), one can make two-phase composites with connectivities ranging from 1-0 to 3-3. A variety of ingenious fabrication processes (some of which mimic natural products) are devised to make these composites. Some of these composites can be extruded as flexible cables.

## 7. Conclusions

Novel methods of preparing starting materials and new techniques of fabricating ceramic products have enhanced the properties of advanced ceramics in some cases and conferred unusual properties in others. As a result, ceramics have become very versatile. Thus, the electrical behaviour of ceramics ranges from being excellent insulators to electronic and ionic conductors and more recently to high temperature superconductors. While most ceramics are still mechanically weak and brittle, special ceramics are amongst the toughest, strongest and hardest materials available today. It looks as though civilisation has made a full circle, starting with clay-based ceramics at the beginning and having come to advanced ceramics at the present.

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