

## INSA MATERIALS SCIENCE PRIZE LECTURE 1995\*

### SCIENCE AND ENGINEERING OF NON-METALLIC MATERIALS

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When the understanding gained over the last many decades regarding the structure-processing-properties correlation in metallic systems was extended to non-metallic materials, new challenges emerged, opening a new frontier of materials science and engineering. Powders of submicron size and of great chemical homogeneity are prepared by sol-gel route and these powders can be sintered at relatively low temperatures. Novel processing methods have emerged such as liquid phase sintering (as in capacitor ceramics) and, *in-situ* oxidation (Lanxide) and gel-casting (to prepare near net shape ceramics). Electroceramics, which constitutes the largest and the fastest growing segment of the advanced materials, cover a wide range of electrical resistivity—from excellent insulators to outstanding superconducting ceramics. The proverbial brittleness of ceramics is overcome in case of transformation toughened zirconia ceramics. Microcracking in the so-called low thermal expansion ceramics is reduced by crystal chemical manipulation of the composition or by controlling the grain size. Similarly, fatigue in electromechanical actuators due to electrical switching can be minimized by using fine grain materials.

**Key Words: Science; Engineering, Materials Science; Non-metallics; Electroceramics; Powder Preparation; Electric Fatigue**

#### Introduction

The author is grateful to the Indian National Science Academy and his professional peers and colleagues in the Academy for the signal honour of awarding the 1995 *Materials Science Prize* to him. I look upon this award as a recognition of the work in materials science carried out by my colleagues and students with small inputs from me. Preparation for this lecture gave me an opportunity to review our work and put it in the perspective of the international advances in this field.

Careful studies of the chemistry and physics of metallic systems over the past several decades illuminated the structure and properties of these materials, so that our understanding graduated from an empirical, qualitative level to more rigorous, semi-quantitative, if not quantitative, appreciation. The elucidation of structure at various levels—macro, micro, atomic and electronic—on one hand and the phase transitions as a function of composition, temperature (and pressure) on the other have contributed significantly in this direction. Detailed studies of deformation mechanisms of these materials under the influ-

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ence of mechanical stresses, and as a function of structure, phases and defects of various kinds, have advanced our understanding of their processing behaviour. This new dimension led to establishing structure-processing-property correlations, which constitute the core of materials science and engineering.

The methods and techniques which proved successful in the case of metallic materials have since been extended to non-metallic materials. In doing so, new challenges were encountered. For example, each non-metallic compound or material consists of two or more species with their characteristic electronic configuration, size and charge. The bonding is directional instead of being uniform as in metals. This influences the packing density as well as deformation behaviour. The occurrence of phases and phase transitions as a function of composition and temperature is a phenomenon common to both metallic and non-metallic systems. In addition to all other defects which are common to both types of materials, non-metallic materials often contain porosity and non-stoichiometry as additional complications. The fact that most non-metallics are brittle makes deformation processes more complicated and consequently a clear understanding of the processing methods employed more difficult. Even in the face of such challenges, there has been sufficient progress to make the science and engineering of non-metallic materials an emerging new frontier. In the following, some of the exciting advances in this field are reviewed with admittedly some bias to the author's own research interests (over the past four decades). New methods of preparation and processing of non-metallic materials are covered, followed by the range of unusual properties displayed by advanced ceramics for new applications.

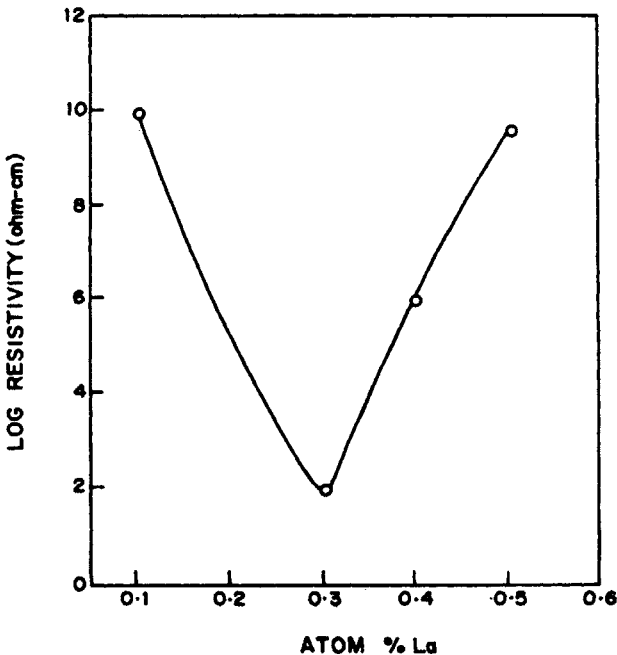


Fig 1 Electrical resistivity of  $\text{BaTiO}_3$  vs % La

## Powder Preparation

Ceramics have traditionally been made by mixing oxides or other compounds (carbonates, nitrates, sulphates, etc.); the latter are decomposed at appropriate temperatures. This solid state mixing approach is responsible for some of the limitations of the resulting ceramic in terms of purity, homogeneity, reactivity, etc. Some of these problems may be minimized, if not eliminated, by using solution-precipitation-decomposition route for powder preparation. Advances in solid state chemistry led to the sol-gel method<sup>1-3</sup>, new precursors, including alkoxides<sup>4,5</sup>, and topochemical reactions<sup>6</sup>. The atomic scale mixing and the resulting homogeneity made possible by these methods enabled the introduction of trace amounts of La (or other rare earths) in BaTiO<sub>3</sub> in a uniform manner. This results in the reduction of electrical resistivity of BaTiO<sub>3</sub> by a factor of 10<sup>10</sup> in positive temperature coefficient of resistance (PTCR) ceramics (Fig. 1). Hydrolysis of zirconium tetrabutoxide in alcohol solution can be used to produce monodispersed ZrO<sub>2</sub> powders<sup>7</sup>. The chemically prepared powder consists of nanometer particles, which sinter to pore free, high density compacts at temperatures several hundred degrees lower than in the case of solid-state reacted powders<sup>8</sup>. The disordered structure of a gel is conducive to the production of amorphous glasses<sup>9</sup>.

While the sol-gel preparation methods offer many advantages such as high purity, great homogeneity, small size, reactive powders with sinterability at low temperatures, it must, however, be noted that the precursors employed are expensive. Therefore, a careful performance-cost analysis needs to be carried out before adopting it for large scale production.

## Processing

The most common ceramic processing techniques include slip casting, dry pressing, extrusion and less frequently isostatic or hot isostatic pressing besides injection molding. The fabricated parts are dried and finally sintered. The various steps in such processing methods result in considerable shrinkage and density gradients, both of which result in microcracking and non-uniform properties. If possible, lower sintering temperatures are also desirable to conserve energy.

In order to address these issues, advances are being made with new processing techniques. Some of these are briefly reviewed here.

1) *Liquid Phase Sintering*: Sintering depends upon diffusion. Enhanced diffusion can reduce sintering temperatures. Diffusion rates are generally higher in liquids than in solids. Therefore, presence of a liquid phase, even if it is small in quantity and transient in nature, can result in substantial lowering of sintering temperature, sometimes by several hundred degrees. For example, a small amount of bismuth borate glass decreases the sintering temperature of barium titanate from about 1350 to about 1000°C, without affecting the dielectric constant<sup>10</sup>. In the case of multilayer capacitors, which are produced by sintering a stack of alternate layers of a dielectric and a metal electrode, the lowered sintering temperature makes possible the use of cheaper silver as electrode mate-

rial in place of expensive palladium alloys. Similarly, a small amount of commercial sealing glass is employed to lower the sintering temperature of relaxor ferroelectric lead magnesium niobate<sup>11</sup>, which has an exceptionally large dielectric constant, which is, however, frequency-dependent.

2) *In-situ Oxidation*; In this novel lanxide process, a component is cast from molten aluminium alloy, followed by controlled oxidation at the moving liquid/solid interface to result in an alumina component of the desired shape and size<sup>12</sup>. The multitude of steps and long period of time and high sintering temperatures normally employed in the fabrication of alumina components is replaced by a single casting-oxidation step which is completed at a lower temperature and in a shorter time compared to conventional processing. This technique is particularly useful to fabricate complex shapes and to achieve near net shape without resorting to expensive grinding and polishing operations, following sintering<sup>13-15</sup>.

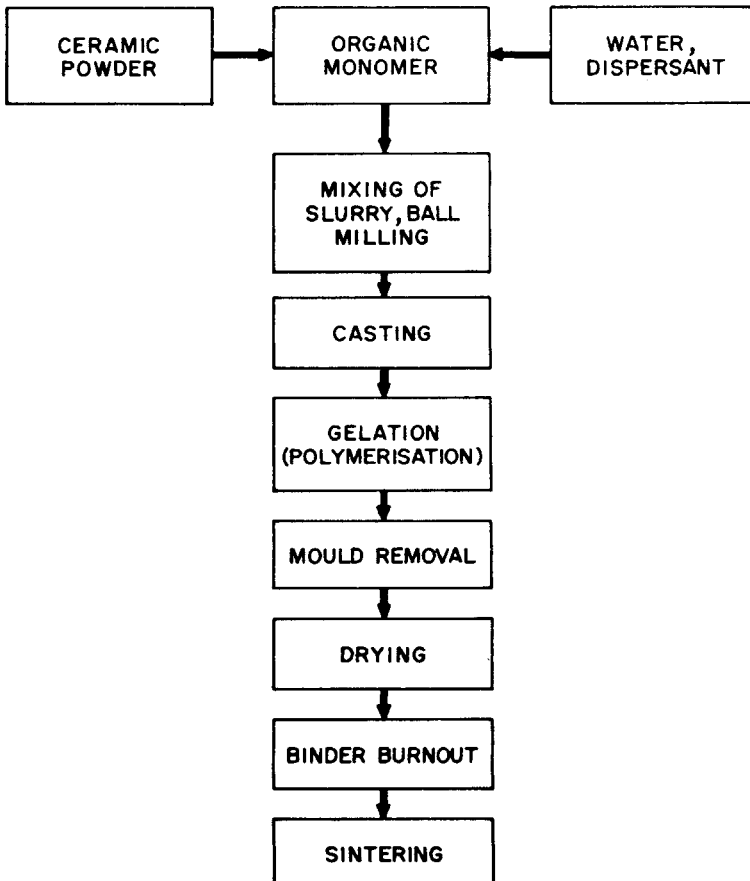


Fig 2 Flow sheet for gel-casting

3) *Gelcasting*: This is an emerging new fabrication process for producing near-net shape ceramic parts<sup>16</sup>. The process flowsheet (Fig. 2) indicates that powders, monomers, an initiator and solvent or water are mixed together and cast in a mold made of metal, glass or plastic. The monomer, on polymerization, provides a strong, cross-linked polymer-solvent gel and permanently immobilises the ceramic slurry in the shape of the mold. The solvent/water can be removed by drying without the migration of the cross-linked polymer with its interlocked ceramic particles. Polymerization can be initiated by irradiation or by the addition of a free radical donor. The challenges of gel casting method, which are currently under study, are to increase the solids content in the slurry in order to minimize the shrinkage during drying and firing and to find less toxic, simpler monomers than the acrylate and acrylamide systems presently in use.

The gel casting method is employed in the laboratory or on a small scale to produce speciality items of alumina, silicon nitride, sialons, alumina-zirconia<sup>17-19</sup>, in aqueous and sometimes non-aqueous systems.

The advantages of the gel casting technique over other ceramic fabrication processes such as injection molding and slip casting are the near net shape achieved, greater green strength, smaller amount of additives, absence of plaster of paris molds which require intermediate drying, fabrication of complex shapes, uniformly dense walls, etc.

### Properties

Some of the new or enhanced properties exhibited by engineering ceramics are reviewed here.

1) *Electroceramics*: Electroceramics constitute nearly 90% of advanced ceramic markets. Generally, ceramics are good electrical insulators, e.g., ferroelectrics. However, substantial electrical conductivity due to movement of ions or electrons can be induced into ceramics; in fact oxide superconductors generated unprecedented excitement in science and technology recently. The electrical resistivity of ceramics is spread over 30 orders of magnitude (Fig. 3). These materials are considered here.

a) *Ferroelectrics*: Barium titanate, BaTiO<sub>3</sub>, is the ferroelectric par excellence for capacitors. The dielectric constant of barium titanate has been enhanced from about 1000 to over 100,000 by employing fine particle material<sup>20</sup> or barrier layers<sup>21</sup>, (Fig. 4) etc. The defect chemistry of barium titanate compositions is so adjusted that capacitors with base metal (e.g., Ni) electrodes can be sintered in an appropriate oxygen-deficient atmosphere without reducing BaTiO<sub>3</sub> or oxidising the electrode<sup>22</sup>. Two other important classes of ferroelectrics are : tungsten bronze type e.g., PbNb<sub>2</sub>O<sub>6</sub> and bismuth oxide layer type,



where Me' = mono-, di- or trivalent ions

Me'' = tri-, tetra-, penta- or hexavalent ions and

$n = 1, 2, 3, 4, \dots$

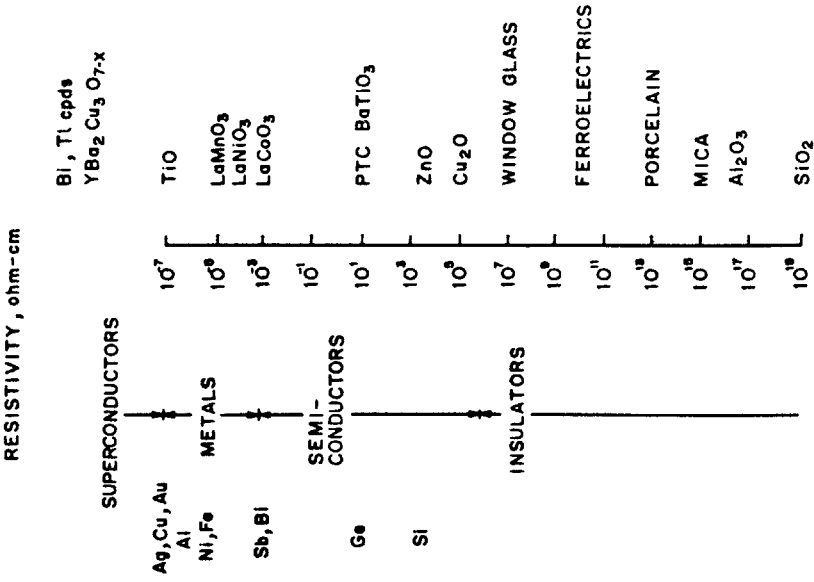


Fig 3 Electrical resistivity of ceramics

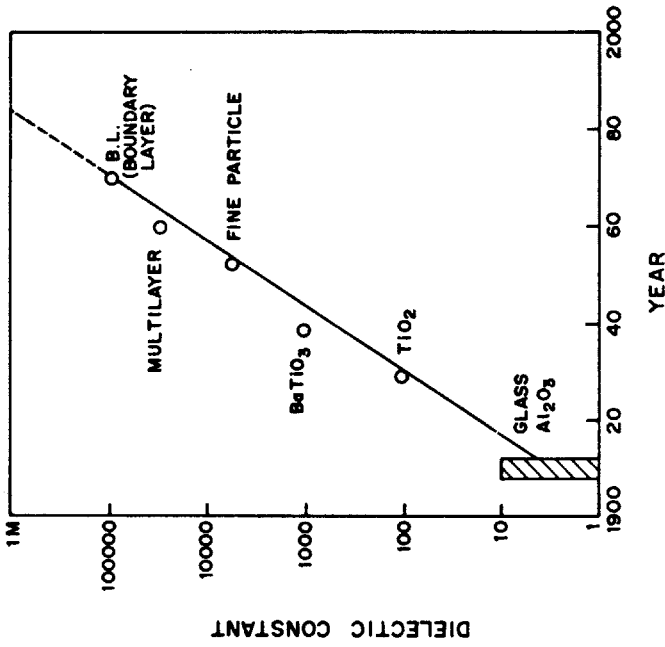


Fig 4 Dielectric constant of capacitor materials over several decades

A morphotropic phase boundary exists in the Pb-Ba niobate system<sup>23</sup> at which outstanding electro-optic properties are exhibited in good quality single crystals. The structure of bismuth layer compounds was shown<sup>24</sup> to consist of layers of  $\text{Bi}_2\text{O}_2$  sandwiching one or more perovskite-like units of  $\text{MeMe}''\text{O}_3$ . A large number of compounds were found to be ferroelectric, some with very high Curie temperatures<sup>25-27</sup>. Some members of this family (e.g.,  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ) have exceptionally low distortion at the ferroelectric-paraelectric phase change and exhibit negligible degradation (fatigue) in ferroelectric properties (polarization and coercive field) even after  $10^9$  cycles of electrical switching. These characteristics make such materials attractive for non-volatile memory devices (e.g., DRAM's).

b) *Superconductors*: Since the discovery of the superconductivity in 1911, the superconducting transition temperature gradually inched upto 23K in the next 4 to 5 decades. Then, in 1986, Bednorz and Muller discovered superconductivity in a rare earth-Ba-Cu oxide with a  $T_c$  upto 36K<sup>28</sup>. This epochal discovery generated one of the most intense activities in the field of condensed matter, which quickly revealed a number of superconducting compounds such as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , Bi-Sr-Ca copper oxides, Tl-Ba-Ca copper oxides with transition temperatures ranging upto 130K<sup>29-33</sup> (Fig. 5). The importance of this development lies in the fact that superconducting devices based on these oxide materials can function when cooled by liquid nitrogen instead of the earlier metallic and intermetallic materials which required cooling by the more expensive, scarce helium. In order to produce reliable devices with adequate current carrying capacity, detailed extensive effort has become necessary to explore novel methods to prepare the material in thin film and bulk forms, to control oxygen stoichiometry, to achieve grain orientation to optimise the anisotropic properties, to understand interfaces, etc. Thus, the potential of these materials is yet to be fully realised in practical devices.

The superconducting oxides bear considerable structural similarity to the bismuth oxide layer ferroelectrics<sup>34</sup>, discussed earlier. The transition metal is copper in the superconductors while it is Ti, Nb or Ta in the ferroelectrics.

c) *Solid Electrolytes*: While electrons are the charge carriers in semiconducting barium titanate, oxides exhibiting metal-like conduction and superconducting oxides discussed above, oxygen ions can become charge carriers to induce significant electrical conductivity by generating appropriate ionic defects in oxides (e.g., doped zirconia) which are otherwise excellent insulators<sup>35</sup>. In Ca-doped zirconia,  $\text{Ca}^{2+}$  and  $\text{Zr}_{4+}$  ions occupy the cation sites in a fluorite lattice, while the charge balance is restored by creating oxygen ion vacancies (equal in number to the  $\text{Ca}^{2+}$  ions)<sup>36,37</sup>. There is a domain of temperature and oxygen partial pressure in which the electrical conductivity of these materials is solely dependent on the oxygen ion vacancy concentration. This characteristic of doped zirconia solid electrolytes finds application in oxygen sensors, oxygen pumps, high temperature fuel cells, etc.<sup>38</sup>. On the other hand, sodium ions are transported freely in two dimensions of the beta alumina lattice, which serves as the basis for high density sodium-sulphur batteries.

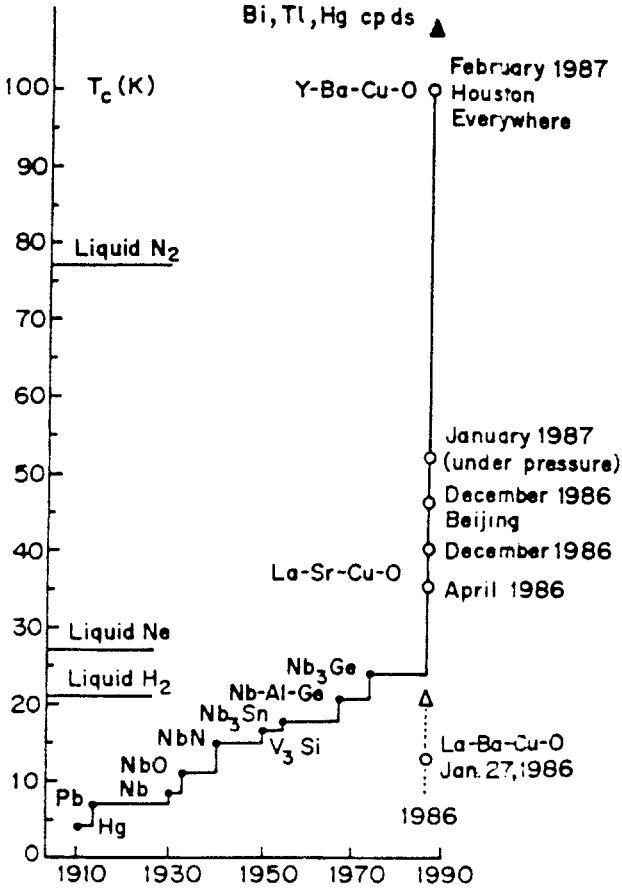


Fig 5 Superconducting transition temperatures of intermetallics and ceramics

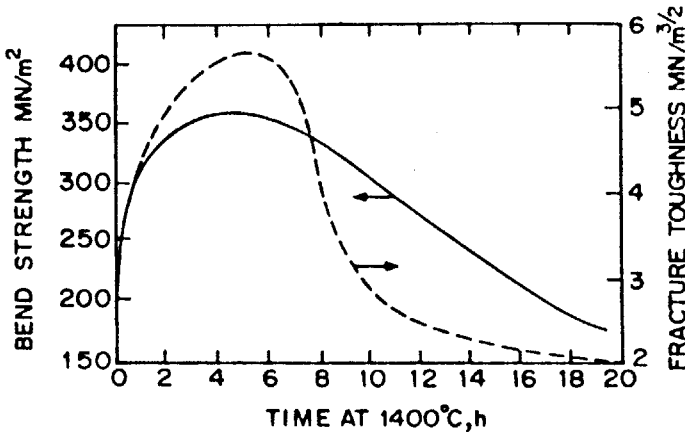


Fig 6 Fracture toughness and strength of zirconia ceramics as a function of annealing time



2) *Structural Ceramics*: The brittleness of ceramics is almost proverbial and has certainly limited its use in structural applications. However, the occurrence of a martensite-type phase transition<sup>39</sup> (tetragonal to monoclinic) in pure and doped zirconia has enabled the production of transformation toughened zirconia ceramics, analogous to TRIP steels. The precipitation of a desired number of tetragonal zirconia nuclei can be achieved by programmed cooling of doped zirconia from high temperatures. The tetragonal zirconia platelets are then grown to an optimum size by annealing at an appropriate temperature for the requisite time (Fig. 6). The fracture toughness of zirconia ceramics is enhanced to a remarkable extent by the presence of tetragonal zirconia platelets (Fig. 7) so that such a material is christened as ceramic steel<sup>40</sup>. Such toughened zirconia ceramics find application as extrusion dies (for hot metals) which outperform tool steel dies to a substantial extent<sup>41</sup>.

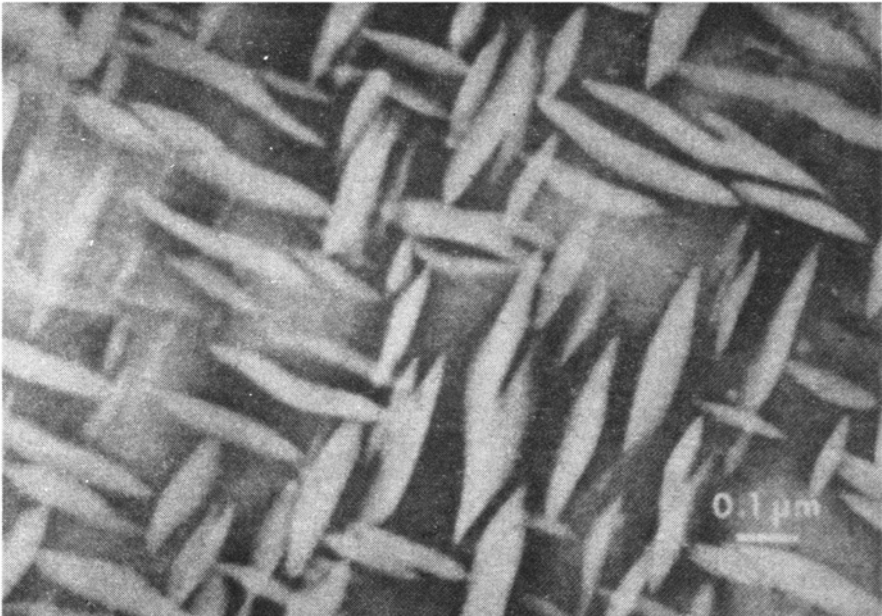


Fig 7 Microstructure of toughened zirconia ceramics

3) *Low Thermal Expansion Ceramics*: While most oxide ceramics have moderate to high thermal expansion coefficients, a few materials (e.g., aluminium titanate, niobia, beta eucryptite, cordierite, sodium zirconium phosphates) exhibit low (near zero) bulk thermal expansion coefficients, thereby generating a great interest in these materials for applications in which steep temperature fluctuations are experienced. In actual practice, however, these materials were found to be mechanically weak. The poor strength is attributed to microcracks arising from anisotropic (some positive and others negative, yielding an overall low) thermal expansion coefficients. Buessem<sup>42,43</sup> has pointed out that microcracks arise during cooling from high temperatures and postulated that they heal during heating. The occurrence and, more importantly, the recombination

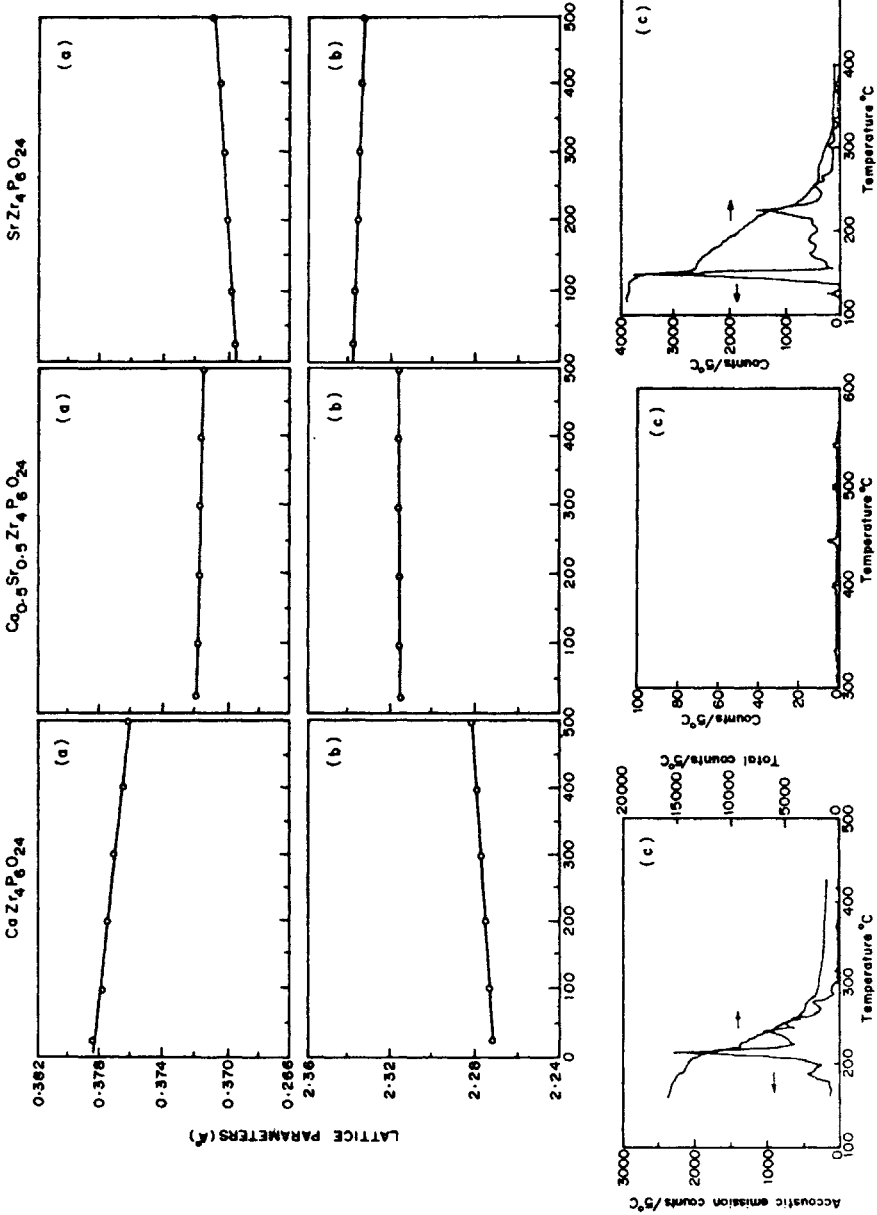


Fig 8 Lattice parameters and acoustic emission of  $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$

of the microcracks has recently been demonstrated through acoustic emission study of niobia<sup>44</sup>, lead titanate<sup>45</sup>, among others. The extent of micro-cracking is limited below a certain critical grain size and becomes prominent with increasing grain size.

The importance of anisotropy of thermal expansion behaviour is established directly in a study of  $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_2\text{P}_6\text{O}_{24}$  ceramics<sup>46</sup>. In one end member (Ca) the  $a$  axis contracts and  $c$  axis expands on heating, while the reverse is true in the other end member (Sr). On the other hand, in an intermediate solid solution composition,  $(\text{Ca}_{0.5}\text{Sr}_{0.5})$ , both  $a$  and  $c$  parameters remain nearly unchanged on heating to 500°C. The acoustic emission study during cooling from 500°C yields considerable acoustic emission activity in the two end members, whereas no acoustic emission activity could be detected in the intermediate solid solution composition (Fig. 8).

### Electric Fatigue

Materials develop microcracks and lose strength when they are subjected to cyclic mechanical loading and unloading. This phenomenon is called fatigue. Piezoelectric materials undergo mechanical deformation under the influence of an electric field and, conversely, develop an electrical voltage when they are subjected to mechanical stress. This property forms the basis for the operation of electromechanical transducers and actuators. However, it has been found that the performance of these devices deteriorate when the electrical field is switched millions or billions of time, causing their poor reliability. A measure of this electric fatigue is a decrease in the reversible polarization and an increase in the coercive field as a function of the number of cycles of electric field switching.

The electric fatigue behaviour of a well-known actuator material, namely lead lanthanum zirconate titanate (PLZT), is studied as a function of grain size (5, 10, 18 and 21  $\mu\text{m}$ )<sup>47</sup>. While no electric fatigue (decrease in polarization or increase in coercive field) is detected in PLZT ceramic with 5  $\mu\text{m}$  grain size even beyond  $10^9$  switching cycles, electric fatigue sets in at lower number of switching cycles as the grain size increases (Fig. 9). This is corroborated by the detection of microcracking under the same experimental condition, using acoustic emission methods.

Using available property values, it is estimated that the critical grain size for fracture in the PLZT ceramic is about 7  $\mu\text{m}$ . This is consistent with the experimental observations of electric fatigue in ceramics with grain size of 10  $\mu$  or large but not when the grain size is 5  $\mu\text{m}$ . This is one more instance of the extension of the understanding gained in metal science to non-metallic materials.

### Conclusions

The understanding gained from the study of the science and engineering of metallic materials has now been extended to the study of non-metallic materials. The underlying differences between these two classes of materials posed new challenges, thus opening up a new frontier in materials science and engi-

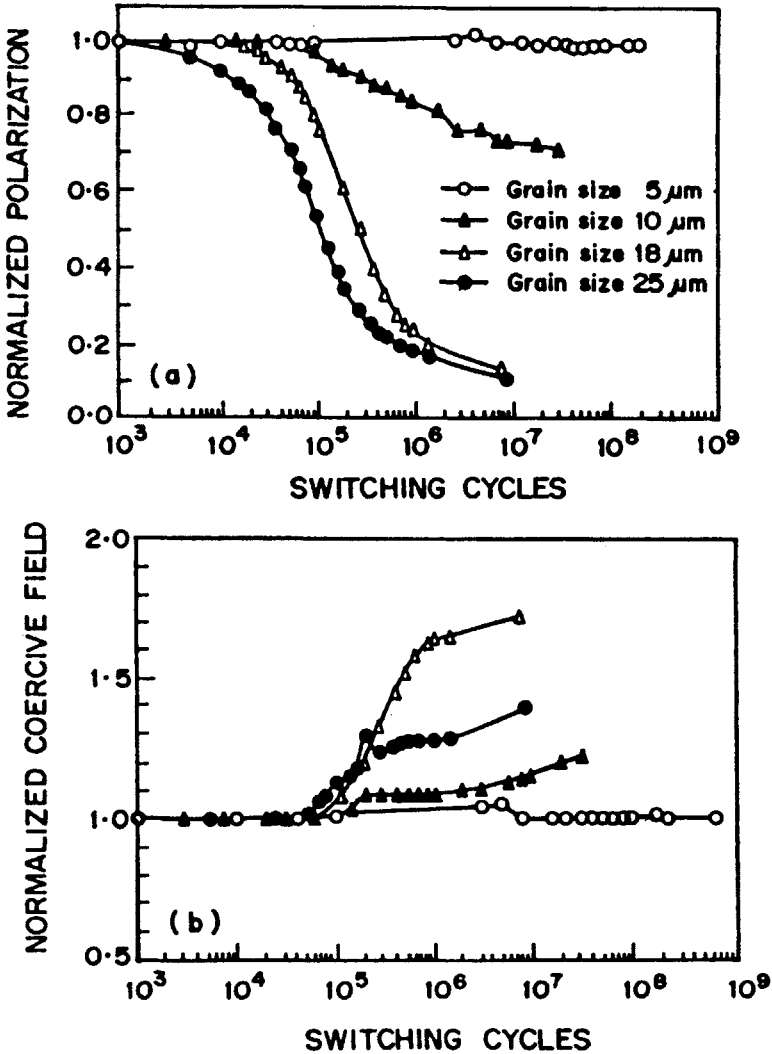


Fig 9 Electric fatigue of PLZT ceramics

neering. The exciting advances being made in processing non-metallic materials and in achieving outstanding properties, including means of overcoming some of the inherent limitations, are discussed. The new understanding gained is enabling the non-metallic materials field to grow at phenomenal rates.

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