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A second ceramic age—A new materials frontier*



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Abstract. A second ceramic age started in the mid-twentieth century as a new, exciting materials frontier. Electroceramics with phenomenally wide range of electrical resistivity (spread over 30 orders of magnitude) span insulators, semiconductors, metal-like conductors, ionic conductors, and, recently, superconductors. They also include ferroelectrics, piezoelectrics, pyroelectrics and electro-optics beside ferrites. Advances in electroceramics have been fascinating and rapid, leading to unprecedented rates of industrial growth. Age-old limitations of poor mechanical strength and brittleness of ceramics are being overcome by outstanding toughness and strength achieved in zirconia-based ceramics exploiting the martensitic transformation at the tetragonal-monoclinic

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phase change. The dimensional changes at this transition which prevented the use of zirconia earlier has now been turned into a mechanism for toughening ceramics to significant levels. Ceramics with near-zero overall thermal expansion coefficient offer new opportunities to science and industry.

Keywords. Second ceramic age; materials frontier; electroceramics; ferroelectrics; ceramic electrolytes; martensitic transformation of zirconia; low expansion ceramics.

1. Introduction

I am most grateful to the Materials Research Society of India for bestowing this signal honour on me to cap my research career. I consider it as a recognition of the quality of the research of my students and associates over the years. I specially cherish this award because it is given by my professional colleagues in the materials research community.

Civilizations are often described in terms of the predominant materials in use, e.g. stone age, ceramic age, iron age, etc. From early times, man has used clay-based products—e.g. bricks, tiles, pots—for shelter, cooking, storage, etc. The universal availability of clay, its plasticity when mixed with water, easy moldability (into shapes) and durability when fired at relatively low temperatures were factors which contributed to the use of ceramics from thousands of years ago. Fired bricks in place of unfired adobe bricks, reinforcing mud walls with natural fibres such as bamboo were later innovations. The accidental discovery of glass-making by Phoenician traders cooking in the Sahara desert gave birth to the glass industry. From further developments in the glass field arose glazes and enamels which added beauty and permanence to pottery. Thus, the old ceramic age produced articles of utility as well as beauty. Ceramic archaeology contributed to our understanding of the evolution of early civilizations.

2. Second ceramic age

Unlike most materials eras, ceramics is having a renaissance, a second life so to say, starting approximately with the second world war, say mid-twentieth century. These new or advanced ceramics build on the accumulated knowledge of the earlier ceramic age but also draw heavily on the basic sciences—physics and chemistry—and advances in engineering—mechanical and chemical engineering, electronics and instrumentation. The blossoming of the new ceramic age is driven by the deeper understanding of materials, processing and properties on the one hand and by the stringent demands of the modern industry on the other.

Advanced ceramics differ from conventional ceramics in many ways (Subbarao 1988a,b):

- processed materials of high purity (e.g. alumina, zirconia) instead of naturally occurring minerals such as clay, sand, feldspar, quartz, etc.
- novel fabrication techniques e.g. doctor blade, isostatic and hot isostatic pressing, injection moulding in addition to conventional cold pressing, slip casting, etc. followed by drying and sintering.
- properties of current interest include mechanical strength, fracture toughness, wear resistance, dielectric, magnetic and optical properties.

- new applications are in dielectric, piezoelectric, magnetic, electro-optic and engine fields compared to refractory, crockery, sanitaryware, sheet glass for conventional ceramics.
- higher value addition and unit prices.
- advanced ceramics depend upon knowledge instead of experience, quantitative in place of purely qualitative evaluation, tailored composition/structure/processing to obtain desired and new properties.

Two other characteristics of the second ceramic age may be noted:

- (i) unprecedented growth. For example, at least ten ceramic companies in Japan had phenomenal growth rates of 50–100% during the period 1978–80 (Kenny and Bowen 1983). The sale of advanced ceramics in Japan is projected to grow from \$ 400 M in 1977 to \$ 2,600 M in 1986, \$ 5,900 M in 1991 and \$ 12,100 M in 1995.
- (ii) electronic ceramics constitute nearly 90% of advanced ceramics sales at present and in the foreseeable future, with cutting tools coming second with about 7% (Schober 1987).

In a recent report, the US Department of Commerce has identified 12 emerging technologies; an emerging technology is defined as one in which research has progressed far enough to indicate a high probability of technical success for new products and applications that might have substantial markets within the next ten years. The 12 emerging technologies are divided into four categories, with their expected value in USA in the year 2000 (MRS Bull 1990):

Materials \$ 155 billion;
Electronics and information systems \$ 148 billion;
Manufacturing systems \$ 30 billion; and
Life sciences applications \$ 23 billion.

Advanced materials thus constitute about 40% of the output of all the emerging technologies, and are by far the largest single entity. Advanced materials in this context include structural and functional ceramics, ceramic- and metal-matrix composites, intermetallic and light alloys, advanced polymers, surface-modified materials, diamond thin films, membranes and biomaterials. Products of the second ceramic age cover electrical, magnetic, optical, chemical, mechanical, biological and nuclear functions.

The excitement in the field of advanced ceramics is captured in the following sections through specific examples. The choice of the examples is clearly subjective, with a strong bias towards the author's research interests over the past four decades.

3. Electroceramics

It has already been pointed out that about 90% of advanced ceramics serve electrical functions at present and the trend is expected to continue also in future. This is understandable, since ceramics exhibit a great diversity of electrical behaviour. For example, they possess a wider range of electrical conductivity (over 30 orders of magnitude) than metallic or polymeric materials and span:

- Insulators : alumina, porcelain, glass, ferroelectrics, piezoelectrics, pyroelectrics, electro-optics.
- Semiconductors : ZnO, Cu₂O, doped BaTiO₃
- Ionic conductors : doped ZrO₂, β Al₂O₃
- Metal-like conductors: LaCoO₃, LaNiO₃
- Superconductors : YBa₂Cu₃O_{7-x'}
[(Bi, Tl)₂Ca_{n-1}]Sr₂Cu_nO_{2n+4}

A few examples are now examined in some detail:

3.1 Ferroelectrics for capacitors

In the following, ferroelectric materials are discussed exclusively, to sketch some of the outstanding advances made over the years. Ferroelectrics form the basis for ceramic capacitors, which constitute over 90% by quantity and over 35% by value of all electroceramics produced. To keep up with miniaturization of electronic circuitry over the years, the dielectric constant of the ceramic dielectric used in capacitors has steadily increased from about 100 for TiO₂ to about 1500 for BaTiO₃ to higher values for fine grain and boundary layer materials over a period of time (figure 1). Grain growth of BaTiO₃ is inhibited by the incorporation of a small quantity of Nb or Ta in place of Ti (Subbarao 1959). The high dielectric constants observed in this case are attributed to the fine grain size. Later it has been shown that stresses acting on fine grains clamp domain motions and thereby enhance the dielectric constant (Goswami *et al* 1966). An improvement of ageing characteristics (i.e. degradation of dielectric properties with time under applied electric field) has also been reported in these materials (Buessem and Tropokowicz 1976). A similar approach of adding Nb (<0.5%) made it possible to produce dense, strong PbTiO₃ ceramics by controlling grain growth, though PbTiO₃ ceramics prepared through normal ceramic methods crumbles to powder (Subbarao 1960).

Low temperature and short duration sintering is sought to save energy and to

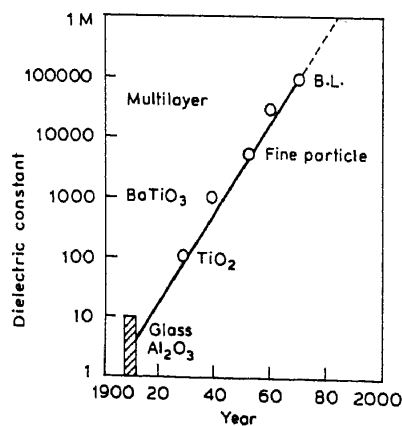


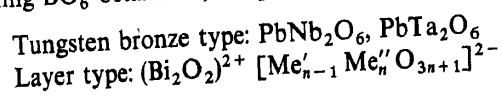
Figure 1. Dielectric constant of capacitor materials over a period of years.

enable the use of cheaper electrode materials than Ag-Pd electrodes conventionally used. It may be recalled that electrodes constitute over 60% of the cost of a ceramic capacitor. Low-temperature sintering can be accomplished by the use of a small quantity of a fugitive liquid (e.g. $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glass) as a sintering aid (Chowdhury and Subbarao 1981) for sintering BaTiO_3 at 1000–1100°C for as short as 10 minutes. The same approach was utilized recently to sinter lead magnesium niobate ($\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$) ceramics to high density at 700–750°C by adding about 1% of a commercial sealing glass, after modifying the glass composition by addition of some magnesium oxide into the glass (Srikanth and Subbarao 1991). The addition of MgO to the glass is to prevent leaching of MgO from the dielectric. PMN composition by the glass, so that an undesired pyrochlore phase of low dielectric constant does not form. PMN belongs to a class of relaxor ferroelectrics which exhibit large dielectric constants where the peak value as well as the temperature corresponding to it are frequency-dependent (Cross 1987). A number of other sintering aids such as NaNbO_3 and lead germanate have been employed in the sintering of ferroelectric ceramics.

In the production of multilayer capacitors, alternate layers of a dielectric and a metal electrode are stacked and co-fired. Therefore, the metal electrode should remain stable under conditions of sintering (temperature and atmosphere). The base metal electrodes (e.g. Ni) which are sought to replace the expensive Ag-Pd alloys, however, oxidize and become poor conductors in the air atmosphere normally used for sintering multilayer capacitors, while the titanate dielectric gets reduced and becomes a semiconductor in a reducing (low P_{O_2}) environment required to prevent the oxidation of nickel. This stringent requirement can be met by incorporating Mn into the BaTiO_3 lattice to adjust the defect structure to make BaTiO_3 into an acceptor type material (Desu and Subbarao 1980, 1981). The Mn-doped BaTiO_3 remains stable under the low oxygen partial pressures required by nickel electrodes.

3.2 Other ferroelectrics

The discovery of ferroelectricity in BaTiO_3 in Japan, USA, and USSR during the second world war was a landmark, since compared to older ferroelectrics such as Rochelle salt, potassium dihydrogen phosphate (KDP), BaTiO_3 is stable over a wide range of temperature, humidity, etc. has a simple perovskite (ABO_3) structure and can be produced in a single-crystal form as well as in a ceramic form in many shapes. Intense worldwide research (Jona and Shirane 1962) led to a number of new ferroelectrics based on substitutions for the A and B ions in the ABO_3 perovskite lattice (e.g. KNbO_3 , PbTiO_3 and also antiferroelectrics such as PbZrO_3 , NaNbO_3). The key to ferroelectricity (and antiferroelectricity) in the ABO_3 lattice was found to be the existence of BO_6 octahedra which are linked through corners to form a three-dimensional network, the cavities in which to accommodate the larger A ion. The B ion is typically small (around 0.07 nm), highly charged (Ti^{4+} , Nb^{5+} , Ta^{5+} , etc.) and occupies an off-centre position in the BO_6 octahedron under appropriate conditions to give rise to a polar state. Armed with this knowledge, ferroelectricity was found in a number of other structure types, bearing a relationship to perovskite structure or containing BO_6 octahedra, the prominent ones being:



where Me' = mono-, di- or trivalent ion
 Me'' = tri, tetra, penta or hexavalent ion and
 n = 1, 2, 3, 4,

PbNb₂O₆ has the distinction of a high Curie temperature (560°C). Partial ionic substitutions (Subbarao *et al* 1960; Subbarao 1962) (e.g. Ba or Sr for Pb, Ta for Nb) have produced a number of useful materials, particularly for electro-optic and piezoelectric applications. Some of our early compositional and structural work revealed morphotropic phase boundaries in some solid solution systems such as Pb-Ba niobates (Subbarao *et al* 1960). Good optical quality crystals of some of these materials have since been produced for electro-optic applications. Smolenskii *et al* (1959) reported ferroelectricity in PbBi₂Nb₂O₉. Following this, a large family of ferroelectrics have been found in this family (Subbarao 1961, 1962a, b) which has a layer-type structure with perovskite type units sandwiched between Bi₂O₂ layers. The crystal structure has been determined by Aurivillius (1949, 1950) for this generic family.

Some examples of this large family are listed in table 1 together with their ferroelectric Curie temperatures. Some of the compounds exhibit exceptionally high

Table 1. Ferroelectric curie temperature of Bi-layer compounds (Bi₂O₂)²⁺ (M_{n-1} R_n O_{3n+1})²⁻.

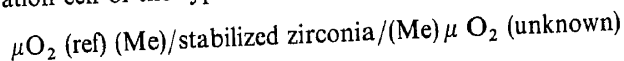
n	M	R	Compound	T _c (°C)
1	-	W	Bi ₂ WO ₆	935
2	Bi	Ti, Nb	Bi ₃ TiNbO ₉	940
	Bi	Ti, Ta	Bi ₃ TiTaO ₉	870
	Ca	Nb	CaBi ₂ Nb ₂ O ₉	625
	Ca	Ta	CaBi ₂ Ta ₂ O ₉	575
	Pb	Nb	PbBi ₂ Nb ₂ O ₉	550
	Pb	Ta	PbBi ₂ Ta ₂ O ₉	430
	Sr	Nb	SrBi ₂ Nb ₂ O ₉	440
	Sr	Ta	SrBi ₂ Ta ₂ O ₉	310
	Ba	Nb	BaBi ₂ Nb ₂ O ₉	200
	Ba	Ta	BaBi ₂ Ta ₂ O ₉	110
	K, Bi	Nb	K _{0.5} Bi _{2.5} Nb ₂ O ₉	435
3	Bi	Ti	Bi ₄ Ti ₃ O ₁₂	675
	Pb, Bi	Ti, Nb	PbBi ₃ Ti ₂ NbO ₁₂	290
	Ba, Bi	Ti, Nb	BaBi ₃ Ti ₂ NbO ₁₂	270
4	Ca, Bi	Ti	CaBi ₄ Ti ₄ O ₁₅	790
	Bi	Ti, Fe	Bi ₅ Ti ₃ FeO ₁₅	750
	Na, Bi	Ti	Na _{0.5} Bi _{4.5} Ti ₄ O ₁₅	655
	Pb, Bi	Ti	PbBi ₄ Ti ₄ O ₁₅	570
	K, Bi	Ti	K _{0.5} Bi _{4.5} Ti ₄ O ₁₅	550
	Sr, Bi	Ti	SrBi ₄ Ti ₄ O ₁₅	530
	Ba, Bi	Ti	BaBi ₄ Ti ₄ O ₁₅	395
	5	Bi	Ti, Fe	Bi ₆ Ti ₃ Fe ₂ O ₁₈
Pr, Bi		Ti, Fe	(Pr, Bi)Bi ₄ Ti ₃ Fe ₂ O ₁₈	~ 780
Pr, Bi		Ti, Fe	Pr ₂ Bi ₄ Ti ₃ Fe ₂ O ₁₈	~ 630
Ba, Bi		Ti	Ba ₂ Bi ₄ Ti ₅ O ₁₈	329
Pb, Bi		Ti	Pb ₂ Bi ₄ Ti ₅ O ₁₈	310
Sr, Bi		Ti	Sr ₂ Bi ₄ Ti ₅ O ₁₈	285

Curie temperatures. There is a renewed interest in this family due to its structural similarity to the bismuth and thallium layer cuprates exhibiting high superconducting transition temperatures (Rao 1988; Subbarao *et al* 1990).

4. Ceramic electrolytes

Unlike other materials in which electrical conduction takes place via either electrons or holes, in ceramics charge transport can also be by ions, both anions and cations. Those materials in which electrical conduction is primarily due to ions are called ionic conductors (Subbarao 1980). In some materials such as doped zirconia, the transport number of anions (which is the fraction of the current carried by oxygen ions compared to the total current carried by all the charge carriers i.e. electrons, holes, anions and cations) is essentially unity in certain ranges of temperature and oxygen partial pressure. Similarly, Na^+ ion is the major charge carrier in $\beta\text{Al}_2\text{O}_3$ ceramics (Subbarao 1980).

Zirconia, ZrO_2 , doped with over 10 mol% Y_2O_3 (or appropriate amounts of CaO , MgO , etc.) assumes a cubic fluorite lattice, in which the cation sublattice is fully occupied by Zr^{4+} and Y^{3+} ions and the charge neutrality is restored by the creation of an appropriate number of oxygen ion vacancies (equal to half the concentration of the Y^{3+} ions) in the anion sublattice (Tien and Subbarao 1963). This results in a high oxygen ion diffusion in yttria-doped zirconia, compared to the diffusion of cations (Y^{3+} and Zr^{4+}). This property is utilized in an oxygen concentration cell of the type



which gives rise to an open circuit EMF, E_0 :

$$E_0 = \frac{RT}{4F} \int_{\mu\text{O}_2 \text{ (unknown)}}^{\mu\text{O}_2 \text{ (ref)}} t_{\text{ion}} d\mu\text{O}_2, \quad (1)$$

where μO_2 is the oxygen potential.

For gaseous atmospheres, one can rewrite equation (1) as

$$E_0 = \frac{RT}{4F} t_{\text{ion}} \ln \frac{P_{\text{O}_2} \text{ (ref)}}{P_{\text{O}_2} \text{ (unknown)}}. \quad (2)$$

For $t_{\text{ion}} = 1.0$, equation (2) becomes the Nernst equation

$$E_0 = \frac{RT}{4F} \ln \frac{P_{\text{O}_2} \text{ (ref)}}{P_{\text{O}_2} \text{ (unknown)}} \quad (3)$$

Here R is the gas constant, T the absolute temperature and F the Faraday constant.

The principle of oxygen concentration cell is utilized in oxygen sensors (Subbarao and Maiti 1988; Subbarao 1990a) used in automobile exhausts (Subbarao 1990b), steel melts, boilers and furnaces. An example of oxygen sensor for automobile exhaust is shown in figure 2. The output from the oxygen sensor is fed back to control the fuel/air ratio to achieve optimum combustion in an internal combustion engine. The advantages of the zirconia oxygen sensor are quick and continuous measurement, electrical output signal suitable for control, accuracy, simple design,

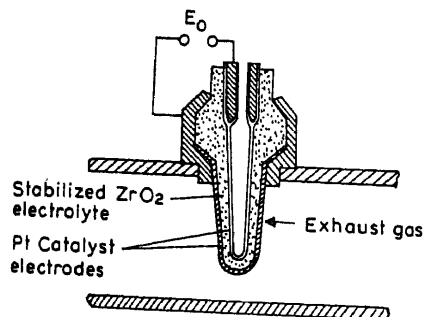


Figure 2. ZrO_2 -based oxygen sensor for automobile exhaust.

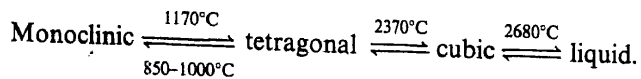
good kinetics due to high temperature operation and weak temperature dependence, while the disadvantages are the high temperature of operation and the cost of the platinum electrode. A single Japanese manufacturer is reported to be producing nearly 800,000 zirconia oxygen sensors per month. The oxygen ion transport through doped zirconia ceramics is also exploited in fuel cells (Maiti and Paria 1988).

The Nernst equation (equation (3)) can also be used to achieve a desired oxygen partial pressure in a flowing gas stream if a voltage dictated by eq. (3) is applied to the oxygen concentration cell operating at a known temperature and a known reference oxygen partial pressure, say air. An oxygen concentration cell operated in this mode is called an oxygen pump (Subbarao and Maiti 1988) and can be used to purify gases and to create known reference P_{O_2} 's (Subbarao 1990b).

The structure of βAl_2O_3 consists of stacks of spinel-type Al_2O_3 blocks, between which some of the cation sites are filled by Na^+ ions. The Na^+ ions are held rather loosely and hence migrate out of the interlayer space quite easily (Subbarao 1980). As a result, βAl_2O_3 ceramic serves as the solid electrolyte separating molten sodium and Na_2S in a Na-S battery.

5. Martensitic transformation of zirconia

Zirconia, ZrO_2 , undergoes a number of phase transitions (Subbarao 1981):



The high melting point of ZrO_2 makes it an attractive refractory material. However, the anisotropic thermal expansion behaviour of the monoclinic and tetragonal phases (Patil and Subbarao 1969) causes crumbling of zirconia ceramics on cooling from the sintering temperature. Addition of oxides of di- and trivalent metals (e.g. MgO , CaO , Y_2O_3 etc.) lowers the transition temperatures of zirconia so that the cubic fluorite phase can be obtained at room temperature. The so-called stabilized zirconia is an excellent refractory material and is also used as a solid electrolyte in oxygen sensors, fuel cells, etc as discussed above.

The tetragonal-monoclinic transformation of zirconia exhibits many of the characteristics typical of martensitic transformations in metals (Subbarao *et al*

1974). These features include diffusionless shear mechanism, existence of a habit plane relating the initial and product phases, athermal kinetics, shape change, thermal hysteresis, etc. Thus, zirconia constitutes an example of oxide undergoing martensitic phase change.

The tetragonal-monoclinic martensitic phase change can be exploited to toughen zirconia ceramics as well as other ceramics (e.g. alumina) containing zirconia. Such transformation-toughened zirconia is christened "ceramic steel" (Garvie *et al* 1975). The toughening process depends upon the size, shape and concentration of the tetragonal phase. Small particle size and rapid cooling of appropriately-doped zirconia can be obtained in fully tetragonal form at room temperature (Gupta *et al* 1977). Such transformation-toughened zirconia ceramics are employed as wear-resistant parts such as extrusion dies for hot metals (e.g. copper, brass and steel). They can also be used as sprayed coatings on metal parts to prevent erosion and oxidation.

6. Low expansion ceramics

Like metals, ceramics (and glasses) exhibit a wide range of linear thermal expansion coefficients (table 2). However, some ceramics exhibit low or near-zero overall thermal expansion coefficient over selected temperature range. This characteristic is exploited in glass-ceramic cookware and in optical components for space applications. All non-cubic materials possess more than one thermal expansion coefficient and often exhibit anisotropic behaviour. In other words, while the overall thermal expansion is small, axial thermal expansion anisotropy can be substantial, resulting in a thermal hysteresis behaviour on cooling and heating. They show the usual contraction on cooling from high temperatures down to a certain temperature followed by expansion on cooling to lower temperatures. The resulting thermal stresses lead to poor mechanical strength of such ceramics. This unusual behaviour is exhibited by aluminium titanate, niobia, magnesium dititanate, β eucryptite,

Table 2. Linear thermal expansion co-efficient of selected materials.

Material	Linear thermal expansion coefficient ($10^{-6}/^{\circ}\text{C}$)
Lead	28.0
Aluminium	24.0
Iron	11.0
Molybdenum	5.6
Tungsten	4.0
Fused silica	0.05
Window glass	7.0
Magnesium oxide	14.0
Alumina	7.0
Aluminium titanate)
Li-Al silicates e.g. β Eucryptite)
Mg-Al silicates e.g. cordierite)
Na-Zr phosphates e.g. $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$)
Niobium pentoxide)
	~ 0.0

sodium zirconium phosphates, alumina and titania, among others. The occurrence of microcracks due to thermal stresses on cooling and their healing on heating were first explained by Buessem *et al* (1952; Buessem 1961) in the case of aluminium titanate. However, direct evidence for microcracking due to anisotropic thermal expansion of aluminium titanate has been obtained only recently via acoustic emission studies (Wright 1972; Ohya *et al* 1987). Roy *et al* (1989) found that the *c* parameter of $\text{CaZr}_4\text{P}_6\text{O}_{24}$ and *a* parameter of $\text{SrZr}_4\text{P}_6\text{O}_{24}$ expand on heating while the *a* parameter of the Ca compound and the *c* parameter of the Sr compound contract on heating. The anisotropic thermal expansion behaviour of the Ca and Sr compounds of the sodium zirconium phosphate (NZP) family causes microcracking on cooling as detected by acoustic emission technique (Srikanth *et al* 1991a) (figure 3). However, the solid solution composition $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ possesses *a* and *c* parameters which remain essentially unchanged on heating through a few hundred degrees. Consequently, this material should not suffer microcracking on heating and cooling. Accordingly, no acoustic emission signals are detected (figure 3). In a study on niobia ceramics, evidence for recombination of microcracks during heating has also been obtained (Srikanth *et al* 1991b).

7. Conclusions

The renaissance or a second age of ceramics based on advanced ceramics started in

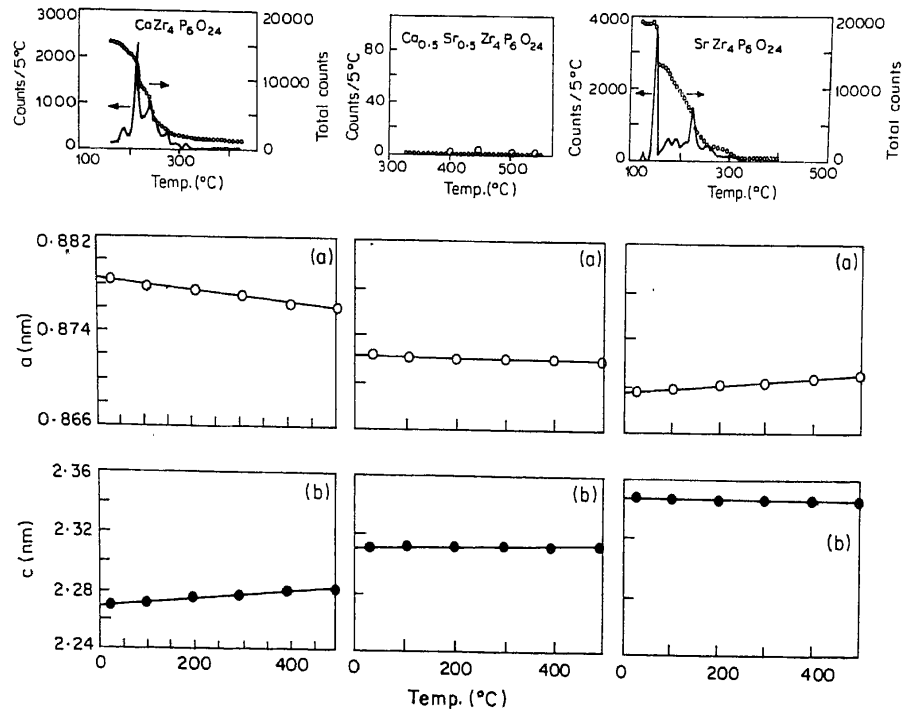


Figure 3. Temperature dependence of lattice parameters *a* and *c* and acoustic emission (total counts and counts/5°C) on cooling from 500°C of $\text{CaZr}_4\text{P}_6\text{O}_{24}$ (left), $\text{SrZr}_4\text{P}_6\text{O}_{24}$ (right) and solid solution composition $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ ceramics (middle).

the mid-twentieth century and is growing at a phenomenal rate. Electroceramics now dominate the advanced ceramics scene and in the foreseeable future, structural ceramics (together with composites based on ceramics), particularly for wear-resistant and engine applications, are expected to grow.

Electroceramics encompass insulators, semiconductors, metal-like conductors, ionic conductors, superconductors besides ferroelectrics, piezoelectrics and electro-optics. The age-old limitations of the brittle nature of ceramics are being overcome by taking advantage of martensitic transformation in zirconia to produce toughened ceramics.

The excitement in advanced ceramics is captured through examples, selected from the author's research in the field of ferroelectrics, ionic conductors, martensitic transformation and low expansion ceramics.

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