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Ferroelectrics: The role of ceramic science and engineering

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Abstract

The key role of ceramic process science in the exploitation of ferroelectric ceramics over the last 50 years is reviewed. Focussing on the development of the most important commercial examples, primarily barium titanate-based capacitors and piezoelectric PZT, the importance of phase equilibria, sintering, defect chemistry and microstructure control are examined. The part played by process science in the increasing significance of ferroelectric thin films and the resurgence of grain-oriented materials is also discussed. The case of multiferroic and magnetoelectric materials is presented as a new challenge poses to ceramic scientists.

Keywords: Sintering; Microstructures-final; Ferroelectric properties; $BaTiO_3$ and titanates; PZT

1. Introduction

Ferroelectric materials[1–3] make a variety of vital contributions to the digital world, from the humble but ubiquitous capacitor, with manufacturing volumes measured in 10^{12} units p.a., to highly sophisticated piezoelectric systems with a €6000 million annual market and growth rates of more than 15% p.a. Their successful exploitation over the last 50 years has been the result of a multidisciplinary effort across fundamental and applied physics and chemistry, through materials science and on to electronic engineering. Whilst the majority of articles published today focus on the physics of ferroelectric materials, their study and exploitation would not be possible without the vital contribution of ceramic science and engineering. It is on this contribution that this review concentrates, with particular reference to those materials having the greatest engineering impact and highlighting the key features of ceramic process science, including phase equilibria, sintering mechanisms, microstructure control and defect chemistry.

2. Barium titanate and capacitors

It is just over 60 years since the discovery[4] of barium titanate ($BaTiO_3$), now regarded as the cornerstone and prototype of the largest family of useful ferroelectrics: the oxide perovskites. The combination of a large A-site ion and smaller B-site ion in this structure allows for an almost infinite variety of simple (ABO_3) and complex perovskites and their solid solutions. This wide compositional tolerance and the strong composition dependence of ferroelectric phase transitions have allowed perovskite ferroelectric ceramics to be exploited in a wide range of applications. An early example of this was the modification of $BaTiO_3$ by isovalent substitutions (e.g. Sr^{2+}_{Ba}),[5] enabling the peak in permittivity at the ferroelectric phase transition to be shifted to room temperature and enabling unprecedented capacitance per unit volume to be achieved. Whilst understanding the origins of these effects falls mainly into the realms of physics, their practical utilization is totally dependent upon ceramic science and engineering. Hence from the late 1940s there was a commercial requirement to produce multicomponent oxides of exceptionally high homogeneity and, given the well-established dependence of dielectric breakdown upon porosity, they needed to be sintered to full density.

In some respects, the sintering behaviour of $BaTiO_3$ represents a rather classic case. At low temperatures, classical models can be applied, suggesting that shrinkage follows $t^{0.3}$ and indicative of an oxygen vacancy grain boundary diffusion mechanism (Fig. 1).[6] At higher temperatures sintering is heavily influenced by the presence of liquid phase. Most $BaTiO_3$ powders tend to be slightly Ti-rich, either deliberately, or due to dissolution of Ba from particle surfaces.[7] The classic $BaO–TiO_2$ phase equilibrium diagram of Rase and Roy (Fig. 2),[8] shows the presence of a 1317 °C eutectic close to $BaTi_2O_5$ (later identified as $Ba_6Ti_{17}O_{40}$; Fig. 3 [9]). Hence, during sintering, a liquid phase

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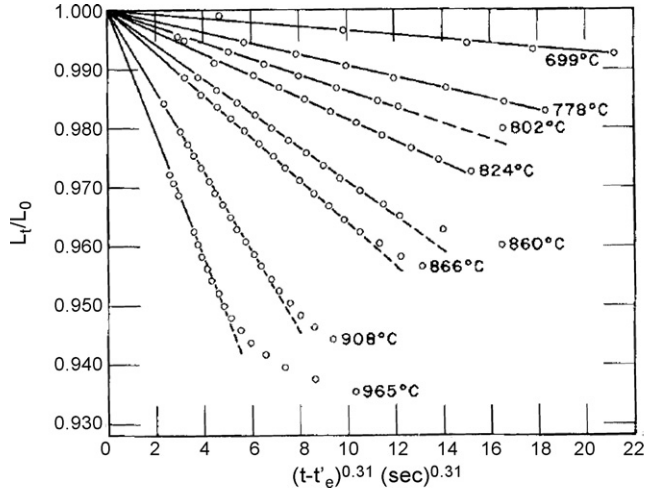

Fig. 1. Early stage shrinkage plots for $BaTiO_3$ (Ref.[6]).

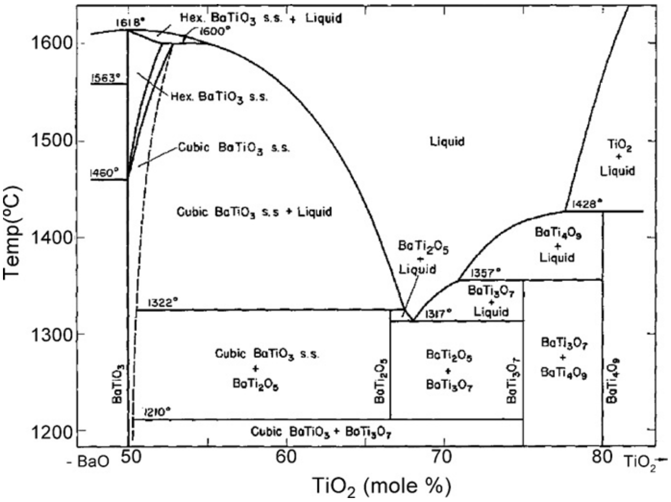

Fig. 2. The $BaO–TiO_2$ equilibrium diagram of Rase and Roy (Ref.[8]).

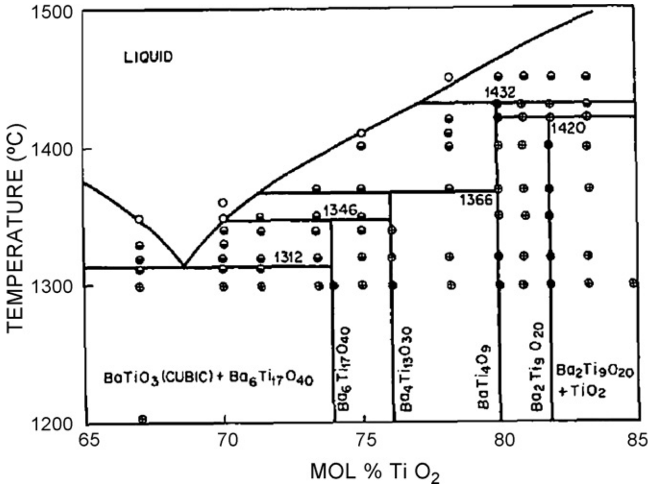

Fig. 3. Revised BaO–TiO equilibrium diagram (Ref.[9]).

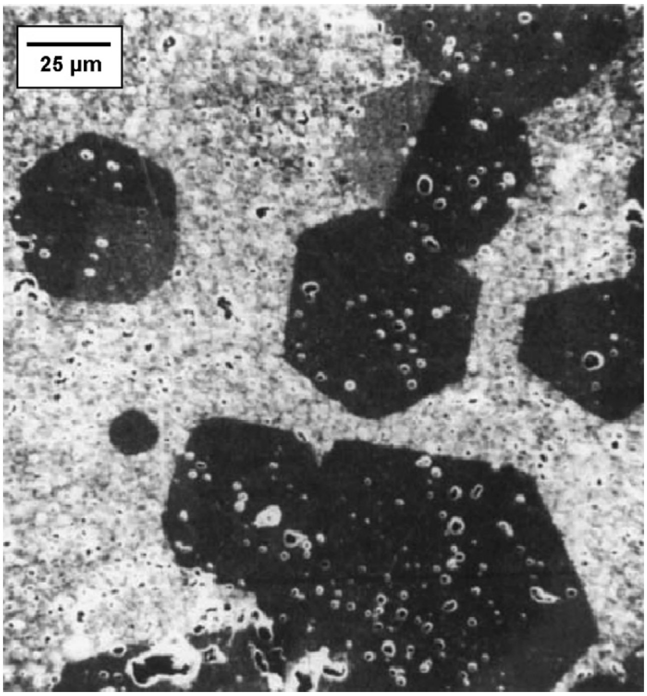

Fig. 4. Coarse-grained microstructure of $BaTiO_3$ exhibiting trapped porosity (Ref.[10]).

is nearly always present and can act to accelerate densification. However, it is also responsible for a solution–segregation mechanism[10] which results in anomalous or discontinuous grain growth and the consequent detachment of pores from the grain boundaries, tending to severely limit the final density (Fig. 4).[10]

The situation is further complicated by the fact that there are in fact two mechanisms of anomalous grain growth. Below the eutectic, prolonged annealing produces large grains which grow parallel to a twin lamella (Fig. 5).[11] Although it was at first thought that the re-entrant lamella boundaries might act to concentrate impurities and thereby reduce the temperature of liquid phase formation, the growth mechanism was later shown to be dependent upon the presence of a solid Ti-rich grain boundary phase (Fig. 6).[12]

It is tempting to say that the sintering and microstructure development of *pure* $BaTiO_3$ is almost irrelevant to the development of modern electroceramics, as all useful $BaTiO_3$-based materials are doped in some way. However, classic studies of the dependence of dielectric properties on microstructure were crucial in pointing the way towards modern dielectric formulations. Several early authors remarked on the high permittivity obtained in fine-grained samples of barium titanate. Egerton and Koonce[13] achieved 1 μm grain size by the then novel technique of fast-firing, with a threefold increase in permittivity over coarse-grained materials (Fig. 7); Anan'eva et al.[14] saw an almost sixfold increase by similar techniques. The origins of this anomalous effect are still discussed over 50 years later and during that period the debate has seen contributions from 3 generations of Leeds alumni: Cross,[15] Payne[16] and Bell.[17,18] However, more than just a scientific curiosity, it has become the phenomenon which underpins modern capacitor dielectrics. The exploitation of this effect in X7R dielectrics required progress

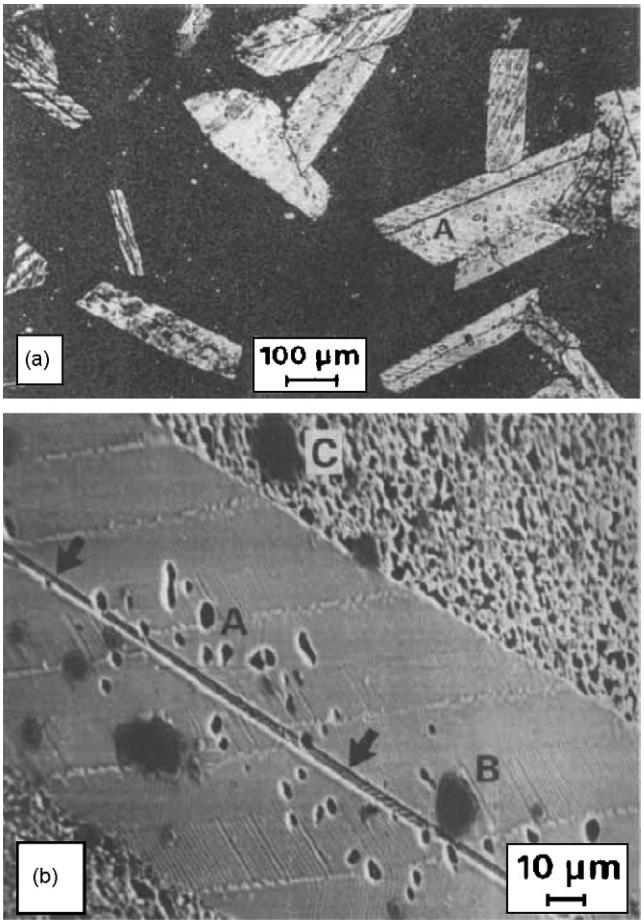

Fig. 5. $BaTiO_3$ ceramic sintered for 100 h at 1250 °C in air. (a) Optical micrograph, showing twin lamellae in large crystallite, e.g. at A, and (b) backscattered electron image of large crystallite containing twin lamella. (Ref.[11]).

in two areas. The first was in defect chemistry. It had been recognized that donor dopants inhibit grain growth,[19] providing a means of exploiting the anomalous grain size effect without exotic thermal processing. However, donor doping also engenders electrical conductivity in $BaTiO_3$. Hence a thorough understanding of the compensation mechanisms by acceptor additions is also required. (The text of Smyth[20] provides a general, but far from exhaustive, overview of the subject.) Somewhat serendipitously, the combination of both donor and acceptor dopants has an even more beneficial influence on the dielectric properties of $BaTiO_3$, producing a concentration gradient in the dopants from the grain boundary to its centre.[21] This has the effect of producing a spatial distribution of Curie temperatures and hence, as temperature changes, the position of the peak in permittivity progresses outwards along the grain radius. This flattens out the temperature dependence of permittivity producing the now ubiquitous "X7R" characteristic for ceramic capacitors (Fig. 8).[22] At room temperature this is manifest as a characteristic "core-shell" microstructure in which only the centre of the grain is ferroelectric, as evidenced by the presence of a ferroelectric domain structure. As the temperature decreases, the boundary between the core and the shell moves outward along the radius. The optimisation of variables such as the Ba/Ti ratio, dopant concentration and thermal treatment for X7R formula-

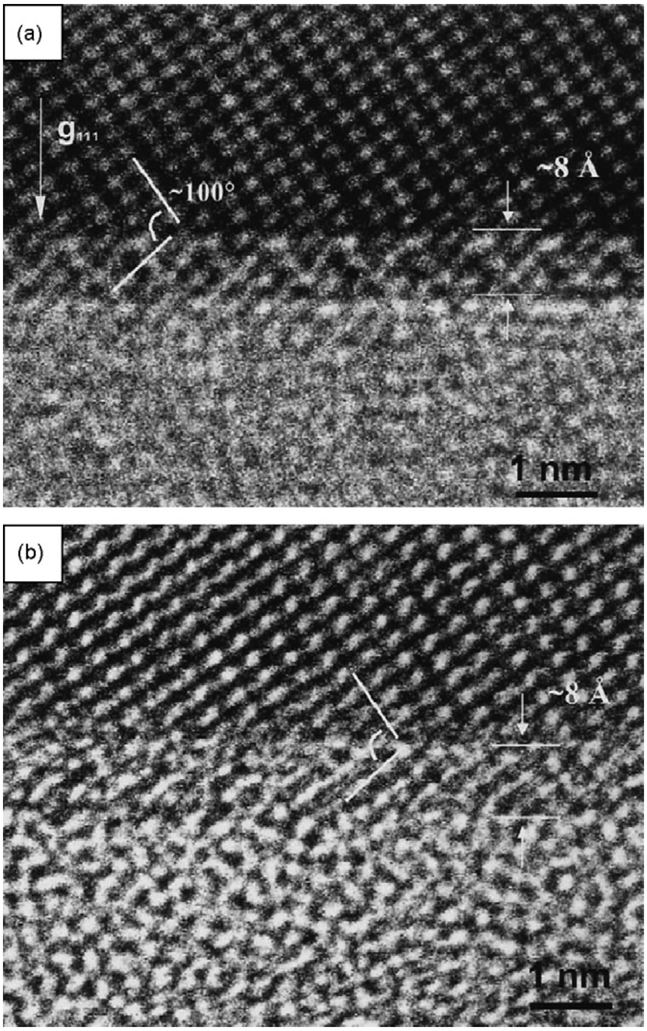

Fig. 6. High-resolution TEM images of the abnormal grain boundaries in low temperature sintered $BaTiO_3$ showing an ordered intermediate phase. (Ref.[12]).

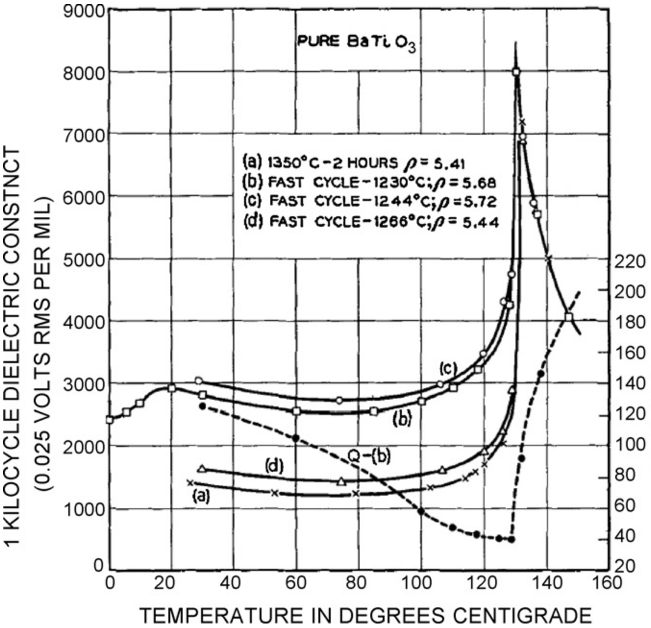

Fig. 7. Dielectric properties of fast-fired $BaTiO_3$ (Ref.[13]).

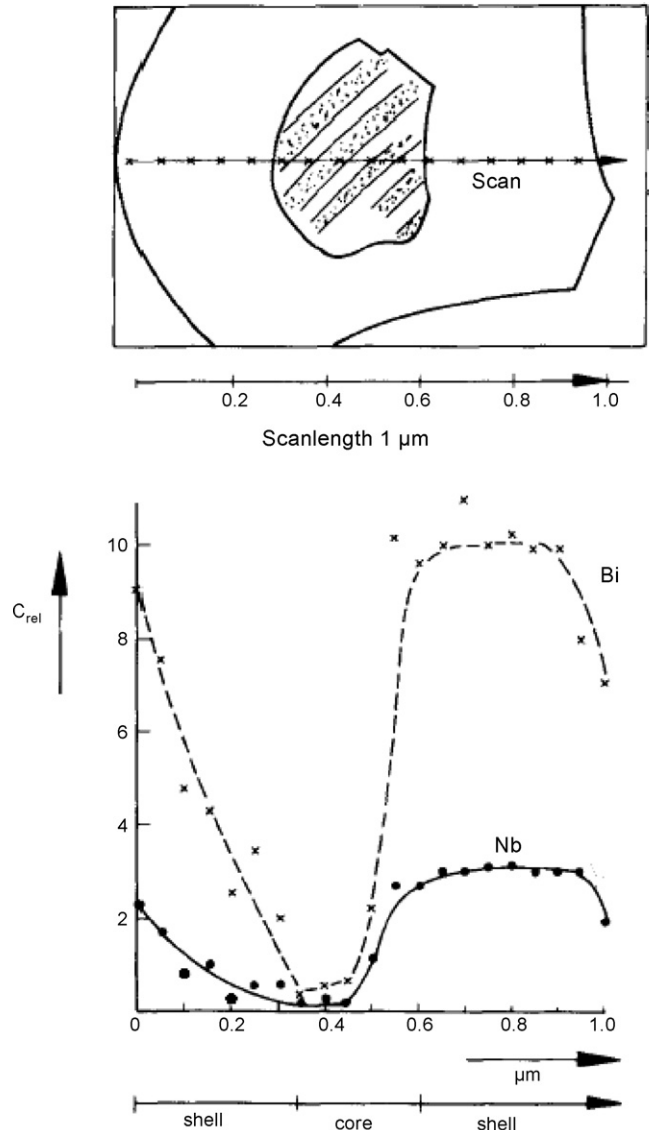

Fig. 8. Schematic diagram of core shell structure and dopant concentrations as a function of grain diameter for doped $BaTiO_3$ (Ref.[22]).

tions, has occupied tens of thousands of man-hours in the last 30 years and will probably continue to do so.

With minor additions (<1 mol%) and fine grain size playing such crucial roles, a large-scale route for producing fine, high purity powders is required. The oxalate route for producing $BaTiO_3$ via precipitation of a barium titanyl oxalate precursor from aqueous chloride solution was invented just over 50 years ago[23] and is one of the earliest examples of what ceramists casually generalize as "chemical processing routes". The elegance of this route lies in the fact that as a mixed cation oxalate, the barium titanium salt is almost unique and precipitates from a highly acidic solution. Hence most common impurities remain in solution and can be washed from the oxalate prior to drying and pyrolysis.

$$\begin{aligned} &TiCl_4 + H_2O \Rightarrow TiOCl_2 + 2HCl \\ &BaCl_2 + TiOCl_2 + 2C_2H_2O_4 \cdot 2H_2O \\ &\quad \Rightarrow BaTiO(C_2O_4)_2 \cdot 4H_2O + 4HCl \end{aligned} \tag{1}$$

Variations of this route are the mainstay of the $BaTiO_3$ industry, producing thousands of tonnes annually for multilayer capacitor production. However, this is a market which is increasingly shared with the hydrothermal routes,[24] which have advantages in terms of lower temperature heat treatments and less agglomeration, but can have the disadvantage of nanoporosity within the crystallites.

In addition to the microstructural engineering required to transform $BaTiO_3$ into a usable dielectric for capacitor use, further elements of ceramic science and engineering are required to engineer the device itself. The maximisation of capacitance per unit volume not only demands high permittivity dielectrics, but requires minimum dielectric thickness. As electronic component design is driven by 2D space optimisation, ceramic capacitors have evolved in a multilayer format, in which the area and volumetric efficiency of the capacitor is minimized by stacking multiple dielectric layers connected electrically in parallel. Tape-casting, or doctor-blading, has been the preferred manufacturing process of the multilayer capacitor (MLC) ever since its inception. Despite a vast literature on the subject, much of it dedicated to improved dispersion chemistry,[25] the modern industrial process is surprisingly similar to that invented by Howatt[26] in 1947 (Fig. 9). Howatt tape-cast ceramics approximately 250 μm in thickness, remarking that when sintered, their dielectric breakdown fields were significantly higher than those exhibited by dry-pressed pellets of the same materials and a testament to the reduction in porosity generally achieved by wet-processing over dry. The intervening years have seen the manifestation of the capacitor equivalent of the semiconductor industry's Moore's law (Fig. 10). $BaTiO_3$ particle sizes are now in the 200 nm range (Fig. 11) and the tape-casting process has been refined until the cast layer thickness today is just less than 1 μm.

Typical multilayer ceramic capacitors (MLCs) often comprise around 300 ceramic layers and so logically must also contain 300 metal layers. The first generation of MLCs employed palladium as the internal electrode layers, due to its oxidation resistance and a melting point higher than the sintering temperature of $BaTiO_3$. However, as layer counts in MLCs increased, the electrode became the dominant cost element of the component and more economic alternatives were introduced. The second generation was based around ceramic compositions with lower sintering temperatures. These were generally achieved by small additions of low-melting point glass frits or fluxes to the existing formulations, thereby lowering the sintering temperature and allowing the use of less refractory (and lower cost) palladium–silver alloys. However, this approach was always at the expense of dielectric performance. A number of manufacturers developed techniques to introduce low melting alloys into the ceramic structure post-firing, however the technique became more limited as the capacitor Moore's law continued its course. The ultimate solution was to use a refractory metal of much lower cost than palladium. Nickel has a sufficiently high melting point, but is incompatible with the oxidizing firing conditions generally used for $BaTiO_3$. However, an answer to this problem had already been identified by Herbert in 1956.[27] If the firing atmosphere were adjusted to allow co-firing of $BaTiO_3$ and nickel without oxidation of the

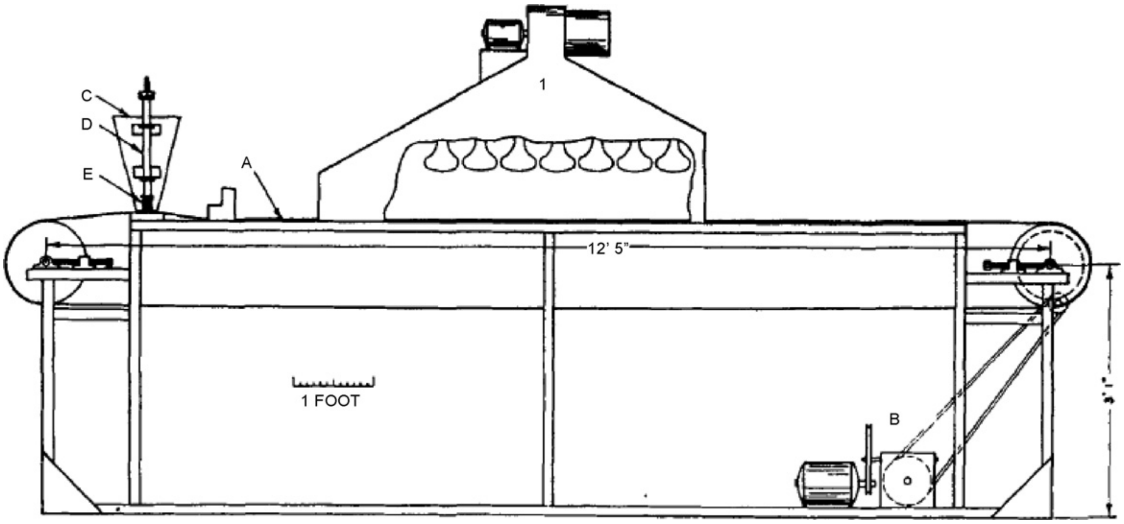

Fig. 9. Schematic diagram of Howatt's original tape-casting apparatus (Ref.[26]).

metal, then the oxygen vacancies created in the ceramic are compensated by electrons reducing the insulation resistance of the capacitor.

$$O_O^x \Rightarrow \frac{1}{2}O_2 \uparrow + V_O^{\bullet\bullet} + 2e' \tag{2}$$

However, in principle, with MnO_2 additions the electrons can be trapped at Mn^{2+} sites which also localize the oxygen vacancies by the formation of a polar defect pair resulting in insulating material:

$$Mn_{Ti}^x + 2e' + V_O^{\bullet\bullet} \Rightarrow (Mn''_{Ti}V_O^{\bullet\bullet})^x \tag{3}$$

This approach was eventually dropped due to breakdown caused by oxygen vacancy aggregation under weak fields, to be replaced by more stable systems based on Ca-doping on the Ti site[28,29] and 3+ amphoteric dopants—those which can either act as acceptors or donors depending upon site occupancy and firing conditions (e.g. Y^{3+}, Dy^{3+}, Ho^{3+}).[30,31]

As dielectric thicknesses are now firmly in the range that were previously thought of as only achievable by vacuum deposition or sol–gel techniques, it is pertinent to ask whether tape-casting will continue to be the process of choice for multilayer fabrication. Given the secrecy that pervades the highly competitive capacitor industry this is a difficult question to answer. The technical issues include not only the process route, but also microstructure property interactions for sub-100 nm grain size. Certainly sol–gel processing is a promising basis for an alternative production route,[32] but whether it can achieve acceptable cost performance compared to current processes remains to be seen.

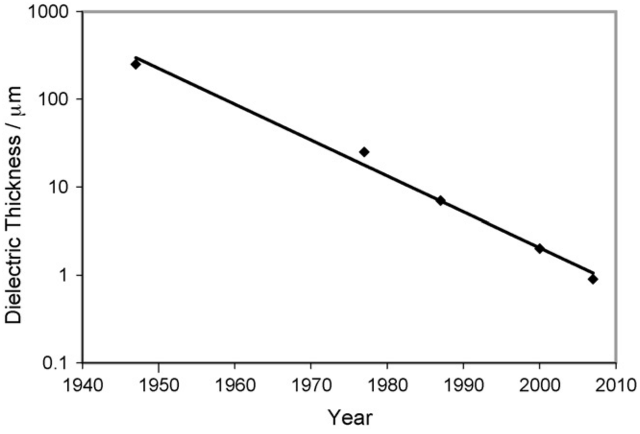

Fig. 10. "Moores law" for multilayer ceramic capacitors.

3. PZT and piezoelectric devices

The second ferroelectric system of major importance is $Pb(Zr, Ti)O_3$ or PZT, which is just over 50 years old.[33] Unlike $BaTiO_3$, which has virtually one application of enormous volume, PZT is truly multifunctional. Besides the plethora of different piezoelectric applications (sensors, actuators, ultrasound,

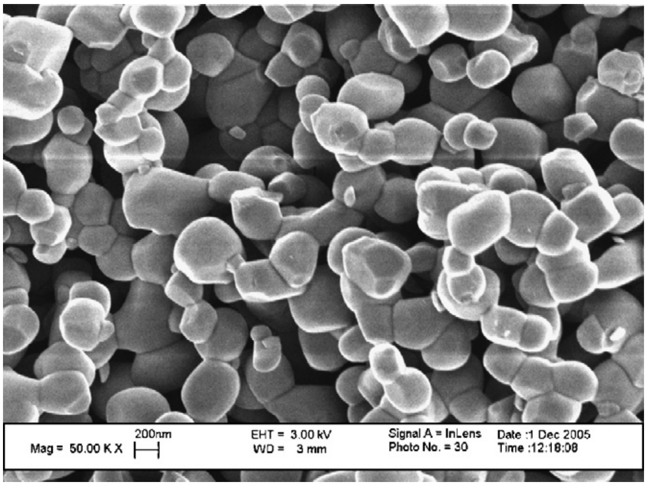

Fig. 11. Typical commercial hydrothermally produced barium titanate powders of ~400 nm particle size.

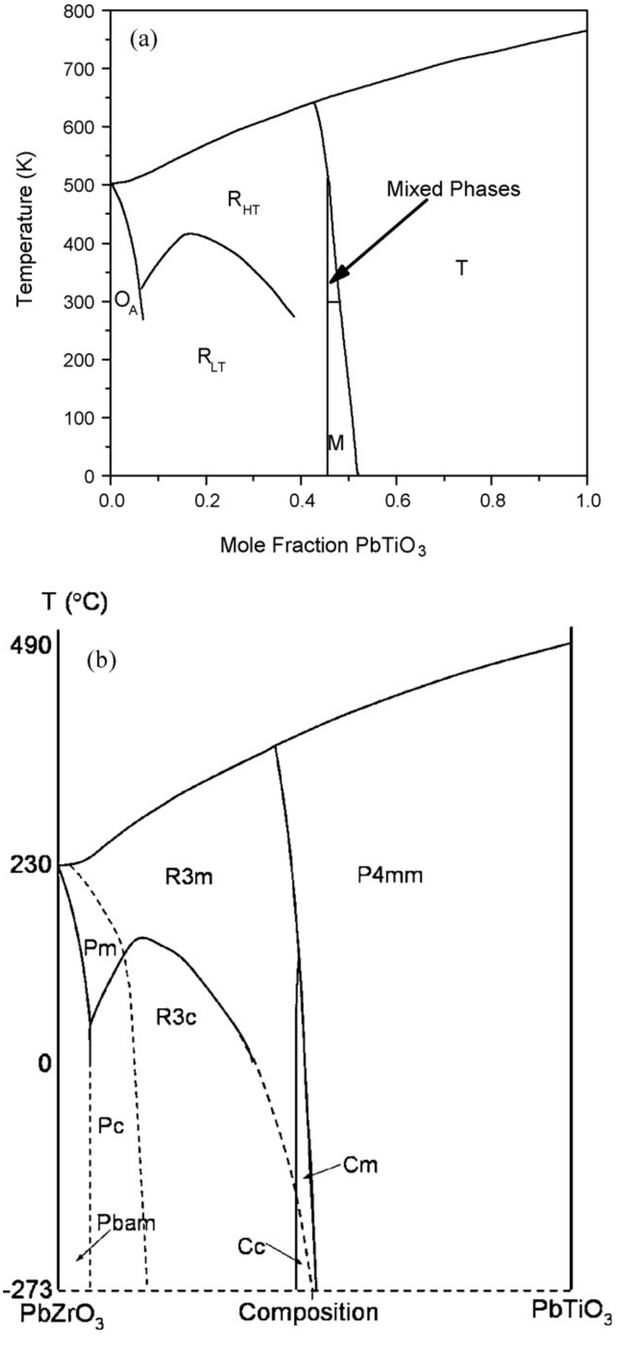

Fig. 12. Sub-solidus phase diagrams of PZT: (a) the conventional diagram modified to showing the relatively recently discovered and still debated monoclinic phase (M) in addition to the rhombohedral (R_{LT} and R_{HT}), tetragonal (T) and orthorhombic (O_A) phases; (b) the proposed diagram of Woodward et al. (Ref.[38]).

transformers and signal processing), it has growing markets in non-volatile semiconductor memories and in pyroelectric infrared sensing and imaging. Moreover, each application demands a slightly different combination of properties. So unlike $BaTiO_3$ dielectrics in which the X7R specification is dominant, PZT has many variants.

It is perhaps surprising that after 50 years, the structure of PZT and the nature of its sub-solidus phase diagram (Fig. 12) is a matter of extensive recent debate.[34–37] Much of the discussion quite rightly focuses on the nature of the so-called morphotropic phase boundary at $Pb(Zr_{0.52}Ti_{0.48})O_3$. It is around this composition that the truly outstanding properties of PZT are found and understanding the origin of this phenomenon is critical to the search for new materials.

However, in terms of ceramic process science, the dominant issue in PZT is the relatively low melting point and high volatility of PbO. As PbO melts at ~890 °C and sintering temperatures are usually in the 1200 °C range, liquid phase is normally present during sintering and the defect chemistry is dominated by Pb and O vacancy formation. Control of these factors is emphasized in key papers by Kingon.[39,40] As in the case of $BaTiO_3$, the presence of a liquid phase can be a double-edged sword. In the initial stages of sintering, shrinkage and densification are accelerated by the presence of the liquid phase. However, if not controlled, rapid particle rearrangement can lead to discontinuous sintering and the appearance of large stable pores. In the latter stage of sintering it therefore appears that the liquid phase inhibits the achievement of full density. On the other hand, lead deficiency can accelerate the final stages of sintering with the Pb and O vacancy concentrations enhancing the solid-state transport mechanisms. Indeed, for those following academic studies and wishing to process reproducible materials to high density with controlled defect levels, a classical solid state sintering route under constant PbO activity, attained by an atmosphere powder of $Pb_{1.1}ZrO_{3.1}$ (not in contact with the sample) is advised. However, in practice most manufacturers have arrived at a process which serendipitously optimises densification rates in both the early and late stages. Sufficient PbO excess is added to the batch to promote liquid phase formation and enhance densification during the early stages of sintering, however as sintering progresses and PbO volatilizes, the system swings into PbO deficit, allowing solid-state mechanisms to complete the job. Nowhere is this more apparent than in the processing of the La-doped, transparent variant, PLZT.

The fabrication of transparent ceramics is a difficult trick to carry of. The minimisation of scattering requires an optically isotropic compound with zero porosity and no grain boundary phases. In terms of ceramic processing, this is sintering perfection and it seems to be achievable in only a handful of systems. In their seminal work, Haertling and Land[41] employed hot-pressing as a means of accelerating pore removal, but also acknowledged the role liquid phase, which given their batching assumptions was almost certainly present in the early stages of heat treatment and from the evidence of the transparency and microstructure of the product, had been eliminated by the end of the process. Their co-worker, Snow, who achieved the seldom repeated feat of producing transparent ceramics by an atmosphere sintering route, discussed the transient nature of the liquid phase in more detail.[42]

In terms of piezoelectric performance the defect chemistry of PZT plays a crucial role in tailoring the characteristics for different types of application. Given that the most commonly occurring impurities in perovskites systems act as acceptors (e.g. Fe, Al) and that their incorporation can be compensated by adding to the background level of oxygen vacancies, there is

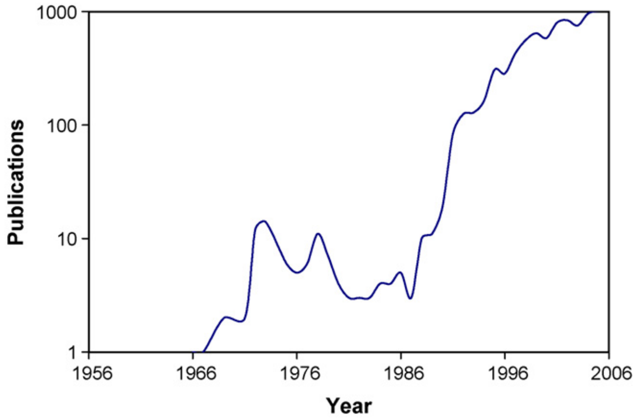

Fig. 13. Number of refereed journal publications per year on the topic of "ferroelectric thin films", (Source: ISI Web of Science).

a propensity in nominally pure material for these to form polar defect pairs.

$$\begin{aligned} &\mathrm{FeO} \Leftrightarrow \mathrm{Fe}''_{\mathrm{Ti}} + \mathrm{O}^{x}_{\mathrm{O}} + \mathrm{V_O}^{\bullet\bullet} \\ &\mathrm{Fe}''_{\mathrm{Ti}} + \mathrm{V_O}^{\bullet\bullet} \rightarrow (\mathrm{Fe}''_{\mathrm{Ti}} - \mathrm{V_O}^{\bullet\bullet})^{x} \end{aligned} \tag{4}$$

The activation energy for oxygen vacancy movement is such that even at room temperature, considerable rearrangement is possible. Hence, the defect pairs can reorient such that their dipole aligns with the local spontaneous polarization with time constants measured in hours. Hence, these defects can inhibit polarization reversal at short time scales, acting as pinning centres for domain wall movement. The action of donor dopants (e.g. $\mathrm{La}'_{\mathrm{Pb}}$, $\mathrm{Nb}'_{\mathrm{Ti}}$) is to reverse this trend, by compensating the acceptors in place of the oxygen vacancies:

$$\mathrm{Nb_2O_5} + \mathrm{V_O}^{\bullet\bullet} \Leftrightarrow 2\mathrm{Nb}'_{\mathrm{Ti}} + 4\mathrm{O}^{x}_{\mathrm{O}} \tag{5}$$

Donor doped materials therefore undergo polarization reversal more easily and, due to their increased domain wall mobility, exhibit increased "extrinsic" contributions to the piezoelectric coefficients, permittivity and dielectric loss. Such materials are known as soft piezoelectrics and typically are used were large outputs are required, e.g. low frequency actuators, and acoustic transducers. Deliberately acceptor doped materials, in which the domain wall pinning is accentuated, are known as hard piezoelectric and due to their much reduced dielectric losses tend to be used in high power, or resonant applications.

4. Thin films

No discussion of ferroelectrics would be complete without reference to the topic of thin films, which today represents approximately 1/3 of all publications on ferroelectricity. As shown in Fig. 13, the interest in this topic was not always so high (note the log scale). However, since the late 1980s, work on the subject has accelerated. The reasons behind this step change in activity are complex, however, a significant factor is process related. Until the late 1980s success in producing films was limited to the few groups employing relatively complex and expensive vacuum deposition techniques; progress was therefore not so rapid. However, the application of sol–gel techniques to ferroelectric thin film fabrication, demonstrated that reasonable quality films could be produced in almost any lab equipped with glassware and a fume cupboard. A seminal paper, by Budd, Dey and Payne, demonstrating the fabrication of PZT films from Pb acetate, Zr and Ti alkoxides in a common solvent of methoxy ethanol was published in British Ceramic Society Proceedings in 1985,[43] and inspired ceramists to become active in a field which until then had been almost entirely populated by physicists. Almost immediately, PZT became the prime candidate for ferroelectric random access memories (FeRAM)[44] and microelectromechanical systems (MEMS)[45] development, supplanting previous intractable materials (e.g. $\mathrm{KNO_3}$[46]). Using the sol–gel technique, rapid progress was made in developing device quality materials, providing ample process related problems for ceramists to solve.[47] Although virtually all of the ~500 million FeRAM devices sold to date have been manufactured by vacuum deposition techniques, without the research contribution of sol–gel films, it is unlikely they would have developed so quickly.

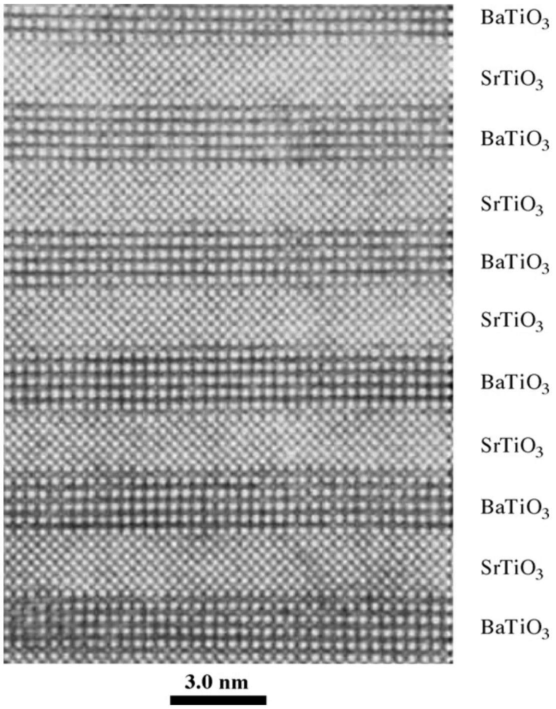

Fig. 14. $\mathrm{BaTiO_3/SrTiO_3}$ superlattice prepared by molecular beam epitaxy (Ref.[49]).

Current work in ferroelectric films focuses on multiferroics (see below), nansocale effects and heterostructures,[48] in which multilayers of alternating compositions are built-up layer by layer on the scale of a few unit cells to attempt to create novel materials through coupling of different physical phenomena (Fig. 14).[49] As epitaxy is of prime importance in these studies, sol–gel techniques are not suited and again vacuum techniques are employed almost universally. However, for applications requiring thick layers of more than 1 μm (e.g. MEMS or pyroelectric sensors), sol–gel can offer a significantly more rapid process route than the vacuum techniques. However, the perennial problem of cracking of thicker films has required significant ingenuity either in sol–gel chemistry[50] or composite film processing[51] for success to be achieved.

5. Grain-oriented ceramics

Research into crystallographically oriented polycrystalline ferroelectrics has been in progress for many years.[52,53] Interest focuses on creating ceramics in which the crystallite polar axes exhibit a very high degree of preferred orientation. This is most easily achievable in materials of which the crystallites or particles naturally exhibit shape anisotropy with a known relationship to the crystal or polarization anisotropy. The most prominent examples are the Bi-layer structure ferroelectrics,[54] the plate-like particles of which can be tape-cast, hot forged,[55] or hot-pressed[56] to produce ceramics with a high degree of crystalline orientation or texture. The polar properties of such materials, primarily the piezoelectric coefficient, are enhanced compared to bodies of the same composition in which the crystallites are randomly oriented.[57] However, except for niche markets, (e.g. exploiting the high temperature properties of lead metaniobate ($PbNb_2O_6$)[58]), the compromise of selecting materials with sufficient shape anisotropy has always resulted in somewhat uncompetitive piezoelectric materials due to their comparatively poor intrinsic properties. The more mainstream perovskite piezoelectric materials, PZT for example, are cubic at high temperature, naturally forming equiaxed particles and for many years were thought to offer no opportunity for grain-oriented processing. However, two relatively recent developments have added greater impetus to producing grain-oriented perovskites. The first was the discovery of extremely high piezoelectric coefficients in Pb-based complex perovskite single crystals[59] and, perhaps ironically, the second was the environmental pressure to reduce the use of lead in electronic materials.

The discovery of piezoelectric coefficients and induced strains an order of magnitude greater than in PZT in single crystals of $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ or PZN–PT and similar materials (e.g. $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ or PMN–PT)[59] produced enormous activity, not only in single crystal research,[60] but also in methods to reproduce these properties in more tractable polycrystalline forms. Due to the lack of shape anisotropy in these materials novel methods, particularly templated grain growth,[61] have been employed. In templated grain growth, rather than attempting to align all particles by tape casting, a small population of seed crystals with large particle size and pronounced shape anisotropy are included in a fine particle matrix of the desired compound. The seeds can be of a different compound as long as they can be shear-aligned, have limited solubility in the matrix and are sufficiently crystallographically similar to provide a substrate for epitaxial growth of the matrix. Successful examples of the technique include the use of $BaTiO_3$ crystals as a template for PMN–PT,[62] with a large number of other systems having been addressed.[63] Texture levels up to 90% can generally be achieved with piezoelectric coefficients 2–3 those of randomly oriented ceramics and 90% of single crystal values. However, the dielectric and electromechanical properties are more hysteretic than those of single crystals. This could be due to clamping by residual template particles, the presence of second phases and a wide orientation distribution.

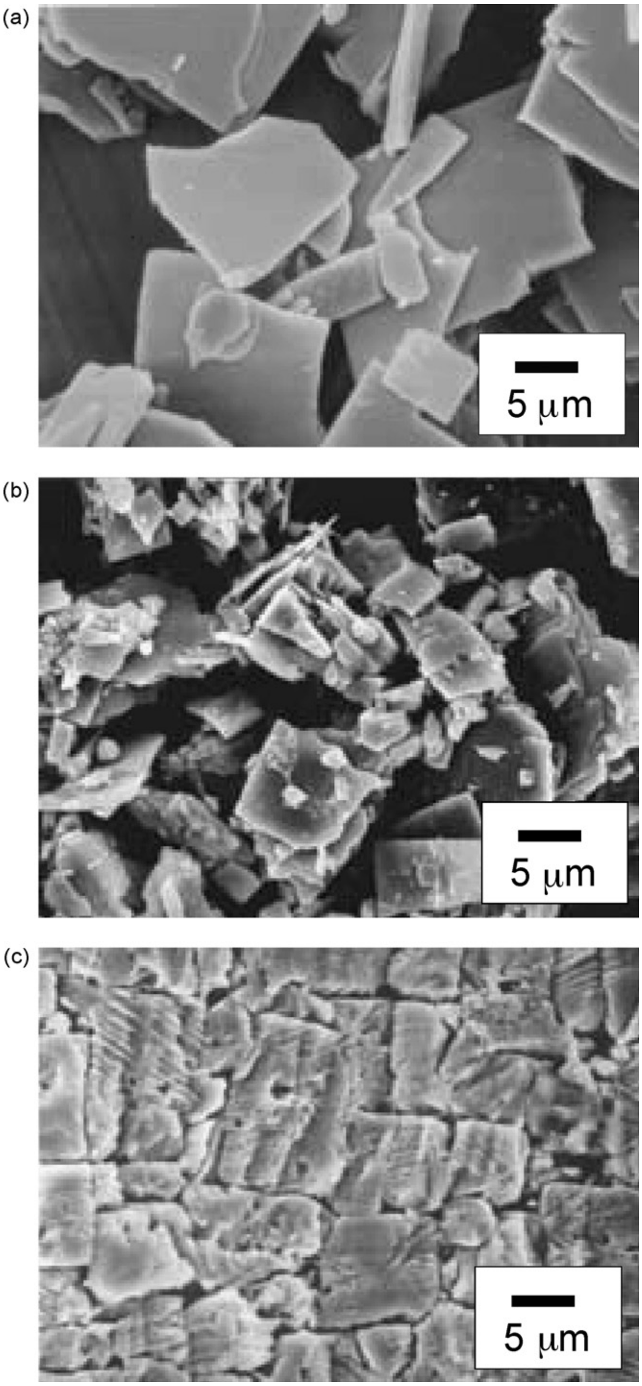

Fig. 15. (a) $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ particles, (b) plate-like $NaNbO_3$ derived by removal of the Bi from (a) and (c) tape-cast $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.10}Sb_{0.06})O_3$ derived form (b), (Ref.[64]).

The introduction of legislation in Europe to limit the usage of heavy metals, particularly lead, in automotive and electronic products, has, despite the waiver currently enjoyed by PZT, led to a world-wide search for lead-free alternatives. This is particularly challenging given that the origin of the spectacular properties of PZT are rooted in the unique nature of the electronic structure of the Pb^{2+} ion. Whilst there are a number of lead-free systems with morphotropic phase boundaries, the most prominent being (K, Na)NbO_3, their piezoelectric properties are poor compared to even an average PZT ceramic. Hence, significant progress has had to be made in grain-oriented processing for them to become competitive. In this case the most successful route has been a return to the tape casting of anisotropic particles of the chosen composition. A two-step topochemical conversion process was used to obtain plate-like particles of a modified (K, Na)NbO_3 perovskite phase from naturally plate-like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ via $NaNbO_3$ (Fig. 15).[64] This method increased the piezoelectric strain at a given field by almost a factor of 2 for this composition (Fig. 16).

6. Multiferroics

The most recent developments in ferroelectrics concern the so-called multiferroics, materials in which more than one ferroic property can be observed. In principle, this includes virtually all the useful ferroelectric perovskites, which exhibit both ferroelectricity and ferroelasticity, however, recently the term has been focused upon those rare materials which are both ferroelectric and ferromagnetic.[65] The challenge is to identify such materials which not only exhibit both effects at room temperature, but which also exhibit significant magnetoelectric coupling.[66] Approaches include both single phase[67] and composite materials.[68] One such system $BiFeO_3$–$PbTiO_3$,[69] presents an interesting challenge for ceramic process science. It is of interest due to its PZT-like morphotropic phase boundary at around 70% $BiFeO_3$ and the potential coupling between this symmetry change and the antiferromagnetic ordering shown by the material. The material is also of interest as a high temperature piezoelectric due to its high Curie temperature at the MPB (>600 °C).[70] The challenge is that close to the MPB, the tetragonal spontaneous strain reaches 18%. A strain of such magnitude is unprecedented in perovskite ferroelectrics and should result in disintegration of polycrystalline bodies on cooling through the Curie temperature (cf. $PbTiO_3$[71]). However, by careful attention to processing, fully dense, tough materials[72] can be produced below the threshold grain size for micro-cracking.[73] More detailed investigation of these materials has revealed a very large range of coexistence of the rhombohedral and tetragonal phases, coinciding with the greatest tetragonal distortion (Fig. 17).[74] It is postulated that the lower cell volume of the rhombohedral material relieves the internal stresses caused by the tetragonal distortion and moreover could act as a toughening mechanism.

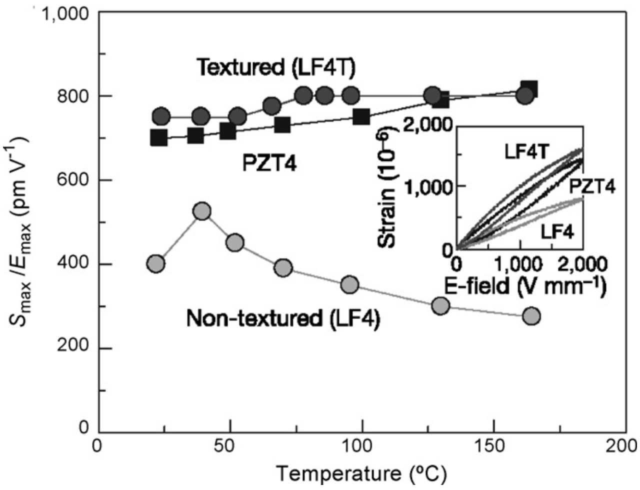

Fig. 16. Comparison of large signal piezoelectric coefficient for textured and untextured $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.10}Sb_{0.06})O_3$ with PZT, (Ref.[64]).

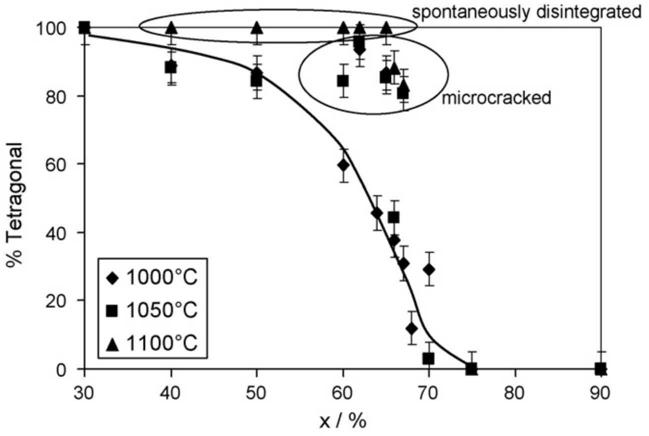

Fig. 17. Volume of tetragonal phase as a function of composition for the $BiFeO_3$–$PbTiO_3$ ceramic system, comparing samples that are high integrity, fully disintegrated and partly microcracked (Ref.[74]).

7. Conclusions

The exploitation of ferroelectric ceramics for a wide range of commercial applications has been shown to be a driver for a number of advances in ceramic process science and engineering. For almost 60 years capacitors based on barium titanate have undergone continuous development, motivated by the need for ever small capacitors. Successive generations have benefited from advances in particle processing, sintering, microstructure control, generations and green forming. The next generation are also likely to benefit from advances in thin film process technology. Piezoelectric applications have experienced a similar history, but with the fabrication of grain-oriented ceramics becoming the current focus of process research.

Recent years have seen enormous growth in the importance of ferroelectric thin films, a phenomenon that owes much to sol–gel research in popularising the subject and making it accessible to a wide range of scientists. The new field of multiferroics is posing novel problems for process scientists in both bulk and thin film forms.

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