

Expanding the application space for piezoelectric materials

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 Andrew J. Bell,  Tim P. Comyn, and  Timothy J. Stevenson

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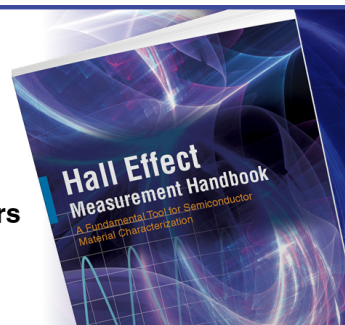
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Andrew J. Bell,^{1,2,a)}  Tim P. Comyn,²  and Timothy J. Stevenson² 

AFFILIATIONS

¹School of Chemical and Process Engineering, University of Leeds, Leeds, United Kingdom

²Ionix Advanced Technologies Ltd, Huddersfield, United Kingdom

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^{a)}Author to whom correspondence should be addressed: aj.bell@leeds.ac.uk

ABSTRACT

The long history of innovation in the field of piezoelectric devices has, over the last 65 years, been predominantly rooted in a single material, the Pb(Zr, Ti)O₃ ceramic, known as lead zirconate titanate (PZT). Despite enormous resources being dedicated in the last 20 years to identifying lead-free alternatives to PZT and developing a thriving, but limited, market in PbTiO₃-relaxor single crystals, most device developments are still PZT based. However, more recently, solid solutions based on BiFeO₃ have opened up new applications for active piezoelectric devices at high temperatures (to 600 °C) and under high stress (exceeding 250 MPa), with applications in industrial ultrasound, aerospace, automotive, and micro-actuators. This perspective article examines how new materials are expanding the application space for piezoelectric materials.

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I. INTRODUCTION

Piezoelectricity was discovered in 1880,¹ and by 1917, the piezoelectric effect in quartz was already being applied in acoustic transducers.² However, after the discovery of ferroelectricity in 1920,³ the larger coupling coefficients of Rochelle salt and dihydrogen phosphates proved to be more attractive for acoustic devices. The discovery of the more chemically stable oxide ferroelectrics, barium titanate^{4,5} and then lead zirconate titanate (PZT)⁶ ceramics, facilitated a step change in piezoelectric technology, and from the 1960s until the early 2000s, the highly customizable properties of PZT enabled the development of new piezoelectric devices to meet a wide range of sensing, actuating, and signal processing requirements.⁷ This growth in applications, and the increasing commercial importance of PZT, has justified materials science research for over four decades, focusing on understanding and augmenting its unique properties.⁸

Although academic interest in PZT has remained strong to the present, around the turn of the century, two developments marked a shift in research on piezoelectric materials. First, the demonstration in 1997 of very high piezoelectric coupling in single crystals of relaxor-PbTiO₃ single crystals⁹ provided a springboard for the

development of commercial materials that offer three times the bandwidth of PZT in sonar and ultrasound applications. Second, the threat of PZT being outlawed by environmental legislation¹⁰ necessitated recruitment of an army of new researchers to the cause of developing lead-free alternatives to PZT. In terms of publication numbers, the latter has proved to be the dominant influence on research; approximately half the current publications on piezoelectricity concern lead free materials. However, the same cannot be said of the influence on industrial activity; currently, the number of commercially available lead-free materials and devices is vanishingly small. This is due to a combination of (i) the inability of industrially feasible lead-free materials to match the combination of properties of PZT used in current devices, (ii) the high cost of redesign of existing devices to employ lead-free materials with different property combinations to PZT, (iii) a complex patent landscape that inhibits commercial entry into the field, and (iv) the continuation of the exemption of PZT from the EU RoHS legislation that otherwise outlaws lead in electronics. The lead-free cause may also have been hindered by materials scientists underestimating the complexity of the material requirements for most device applications.¹¹ Moreover, a number of the leading lead-free candidates are no more environmentally friendly than the PZT they are intended to replace.¹² Hence

the “real-world” impact of research into lead-free piezoelectrics is rather small compared to the existing piezoelectric market.

In contrast, the development of relaxor-PbTiO₃ single crystals has resulted in significant commercial activity with approximately ten companies growing crystals worldwide. The main market for these crystals is in medical ultrasound devices, in which the PZT ceramic has been replaced to a large extent and single crystal is now the preferred material for the development of new transducers with improved spatial resolution.¹³ Naval sonar has also seen significant development activity, with single crystal transducers offering increased sensitivity, wider bandwidth, lower power consumption, and reduced weight compared to PZT-based devices.¹⁴ However, given the long cycle times for the replacement of naval equipment, it is not clear how much of the sonar development has been translated into operational systems. While single crystals may offer significant performance advantages to other sectors, their relatively high price and low maximum operating temperatures have so far discouraged their penetration outside of naval and medical markets.

The piezoelectric market is worth ~\$20b per year.¹⁵ Consistent growth at around 10% p.a., exceeding the underlying growth of the electronics sector, is attributed to increasing innovation in PZT devices, rather than to either of the research themes described above. To a large extent, both of those activities are aimed at replacing PZT rather than expanding the total piezoelectric market. A strategy for stimulating additional growth, by enlarging the parameter space in which piezoelectric materials can operate, has largely been ignored until recently, when there has been some success in developing materials that can operate outside the normal temperature, electric field, and stress limits of PZT. These materials provide solutions to problems that could not previously be addressed by piezoelectricity. In addition, the new materials are extending the viable range of coercive field, depolarization stress, fracture strength, and dielectric strength for piezoelectric ceramics, defining a larger, multidimensional operating space for new applications.

The aim of this article is to assess how research into widening the application space for piezoelectric materials is progressing and whether it has a real-world impact. It focuses primarily on the temperature dimension and on the role of BiFeO₃-based solid solutions.

II. LIMITS TO THE APPLICATION SPACE

Generally, the characteristics of primary importance for selection of a piezoelectric material for a room temperature application are the piezoelectric charge coefficients (d_{ij}), elastic constants (modulus, c_{ijkl} , or compliance, s_{ijkl}), electromechanical coupling coefficients (k_{ij}), dielectric permittivity (ϵ_{ij}), and dielectric loss ($\tan \delta$). Of secondary importance may be the operating/processing temperature range, operating stress, and electric field, as well as the mechanical properties including the coefficient of thermal expansion. For engineers considering materials from outside the mainstream, there is often a large information gap as many research publications only report d_{33} , ϵ_{33} , $\tan \delta$, and the Curie temperature, T_C .

For applications outside the normal operating range of PZT, the depolarization temperature, coercive field, depolarization stress, fracture strength, and dielectric strength may be elevated to be primary parameters in material selection. The first three parameters are all aspects of ferroelectric stability, and their room temperature

values tend to increase with increasing T_C . Hence, identifying piezoelectrics with high T_C not only addresses applications with higher operating temperatures but may also provide materials with greater resilience to a range of other demanding operating conditions.

An appreciation of the temperature dependence of the intrinsic properties of ferroelectric piezoelectrics can be gained from the Landau–Devonshire thermodynamic model of ferroelectrics,¹⁶ from which it can be shown that for a second order ferroelectric transition at T_C ,

$$\begin{aligned} P &\propto (T_C - T)^{\frac{1}{2}}, & \epsilon &\propto (T_C - T)^{-1}, \\ d &\propto (T_C - T)^{-\frac{1}{2}}, & E_c &\propto (T_C - T)^{\frac{3}{2}}, \\ g &= d/\epsilon \propto (T_C - T)^{\frac{1}{2}}, \end{aligned} \quad (1)$$

where T is the temperature. Although the equivalent identities for materials with first-order transitions are more complex, the general trend is the same. The simple model does not have an explicit solution for elastic compliance, but the divergence of permittivity on approaching T_C is controlled by elastic softening; hence, similar divergence is also expected for the compliance. In most cases, this will result in the coupling coefficients (k_{ij}) being somewhat independent of temperature. However, in many materials, the intrinsic behavior is modified substantially by the contributions from ferroelastic domain wall motion. Although the domain wall mobility is temperature activated and therefore expected to increase with temperature, the polarization and spontaneous strain both decrease to zero at T_C ; hence, the extrinsic contributions to ϵ and d will both decline on approaching T_C , moderating the dependence expressed in Eq. (1). Nevertheless, using Eq. (1) as a guide, we can assume that the d coefficient increases with temperature, whereas the g coefficient decreases. Hence, while ferroelectrics may become more effective as actuators and acoustic senders with increasing temperature, they simultaneously lose sensitivity as sensors and receivers. It is worthwhile emphasizing that in a material selection exercise, the d coefficient at room temperature must be taken in the context of the value of T_C and the proposed operating temperature; rejecting high T_C materials on the basis of only modest room temperature performance risks missing a potential class leader.

While theoretically the d coefficient may be a maximum at T_C , experience shows that ceramics tend to depolarize below T_C and therefore have irreversibly lost their piezoelectric properties before T_C is reached. This is a consequence of the temperature activated domain wall mobility; ferroelectric materials become increasingly susceptible to the domains, finding new, randomized equilibrium arrangements under relatively small stresses or electric fields. The temperature at which this occurs is known as the depolarization temperature (T_d) and will determine the maximum operating temperature, T_{max} ($<T_d$). An often-quoted rule of thumb that “ $T_{max} \approx \frac{1}{2}T_C$ measured in centigrade” is clearly a thermodynamic fallacy.¹⁷ In practice, T_d is dependent upon the temperature dependence of coercive field and domain wall mobility and how they are influenced by material defect chemistry. In many commercial materials, the difference between T_d and T_C is of the order of 100 °C; however, in certain cases, it has been observed that $T_d \approx T_C$ or even $T_d > T_C$.¹⁷

A further constraint on operation, somewhat unrelated to the ferroelectric properties, is electrical conductivity. As materials that function essentially in the time and frequency domains, optimal

piezoelectric performance is only achieved at frequencies above that determined by the electrical time constant, $\tau = \epsilon/\sigma$, where σ is the conductivity of the material. For maximum bandwidth, we require σ to be as low as possible; however, in most cases, we can regard piezoelectric materials as doped, wide band-gap semiconductors, in which the conductivity follows the Arrhenius equation. Although ϵ increases toward T_C , the increase in σ with temperature will dominate the time constant in most materials. This is particularly true in oxide perovskites, where oxygen vacancy conduction tends to be present at temperatures above 200 °C. Tailoring the defect chemistry of piezoelectric materials to maintain a low conductivity is therefore a major aspect of expanding the application space.

III. TEMPERATURE PERFORMANCE OF PIEZOELECTRIC MATERIALS

A. Pb(Zr, Ti)O₃

Given the dominance of PZT in the marketplace, it is useful to understand the origins and limits of its performance. PZT is a solid solution between PbTiO₃ ($T_C = 490$ °C) and PbZrO₃ ($T_C = 235$ °C).¹⁸ For the majority of piezoelectric applications, the compositions of interest are close to 52% PbZrO₃ concentration, located within a region of the solid solution noted for a series of complex symmetry changes from the Zr-rich rhombohedral phases via a monoclinic region to the Ti-rich tetragonal compositions.¹⁹ For historical reasons, this is known as the morphotropic phase boundary (MPB), indicating that the transitions are primarily composition-driven, rather than temperature driven. The enhancement of the piezoelectric charge coefficients (d_{ij}) and coupling coefficients (k_{ij}) close to the MPB are attributed to the ease with which the ferroelectric polarization can rotate between the rhombohedral [111] and tetragonal [001] directions,^{20,21} facilitated and augmented by ferroelastic domain wall motion.²² The latter contribution provides a means of optimizing the electrical properties for different types of application.⁸ While high domain wall mobility favors large piezoelectric coefficients and permittivity, it also confers large hysteresis in strain and polarization, increased dielectric loss, and low electromechanical Q . It is believed that polar defect pairs, for example, oxygen vacancies paired with B-site acceptor ions, can impede domain wall motion. Hence, reducing oxygen vacancy concentration by donor doping results in “soft” PZT with large piezoelectric coefficients and higher loss (e.g., $d_{33} = 670$ pC N⁻¹, $\tan \delta = 0.022$, and $T_C = 159$ °C), while acceptor doping increases the defect concentration, reducing the domain wall mobility and providing “hard,” low loss materials at the expense of reduced piezoelectric coefficients (e.g., $d_{33} = 265$ pC N⁻¹, $\tan \delta = 0.003$, and $T_C = 330$ °C).²³

While PZT has proven highly versatile and is present in a wide range of piezoelectric devices, a major constraint is the Curie temperature. In pure PZT, which is rarely employed commercially, T_C around the MPB is in the range 360 °C–390 °C, depending upon the Zr/Ti ratio. However, in the “softest” materials, T_C may be as low as 200 °C. Hence, the maximum recommended operating temperature for PZT compositions extends from around 150 °C to 290 °C. Likewise, the coercive field of PZT, which helps estimate the maximum reverse bias field that can be tolerated before depolarization, is very composition dependent in the range 0.8 MV m⁻¹–1.5 MV m⁻¹. This is analogous for applied stress fields. Soft PZT materials

exhibit depolarization under a uniaxial stress of less than 200 MPa, at which point a phase transition is instigated from the larger volume ferroelectric tetragonal to the ferroelectric rhombohedral state. This de-polarization stress is increased for harder PZT materials, which can be pushed to ~400 MPa at room temperature.²⁴

The dielectric breakdown strength of ceramics is microstructure dependent; hence, even for almost identical compositions, it will vary between different fabrication sources. While commercial suppliers do not commonly report this property, values reported for laboratory specimens of PZT are generally less than 10 MV m⁻¹.²⁵ Similarly, the fracture strength (≈ 100 MPa) and fracture toughness (≈ 1 MPa m^{1/2})²⁶ of PZT are also low when compared to that of other engineering ceramics (300 MPa–1000 MPa and 3 MPa m^{1/2}–10 MPa m^{1/2}), suggesting that there is scope to identify piezoelectric materials with much improved mechanical properties.

Nominally, pure PZT exhibits both ionic (oxygen vacancy) and electronic (holes) conductivity.²⁷ The time constant, τ , drops from around 4 s at 175 °C to ~1 ms at 380 °C, just below T_C , and at 600 °C, it would be around 2 μ s. Donor doping of a level consistent with soft materials can reduce the conductivity by 3–4 orders of magnitude, with similar benefits to the time constant, while acceptor doping tends to increase conductivity by up to an order of magnitude.²⁸ For a fictitious, donor-doped, PZT-like ferroelectric, devices operating up to 600 °C, at frequencies as low as to 5 kHz, would be feasible, below which frequency conductivity would introduce unacceptable power loss.

B. Non-ferroelectric and non-perovskite high temperature piezoelectrics

These materials were the subject of a comprehensive review by Zhang and Yu in 2011,²⁹ from which the data are summarized here, unless otherwise stated. The piezoelectric coefficients given are at room temperature.

Non-ferroelectric piezoelectrics possess the distinct advantage of not being limited by Curie temperature. On the other hand, such piezoelectricity can only be exploited in the single crystal form. These materials include quartz and its analogues (AlPO₄, GaPO₄, and GaAsO₄), langasite (La₃Ga₅SiO₁₄) and its isomorphs (La₃Ga_{5.5}Nb_{0.5}O₁₄ and La₃Ga_{5.5}Ta_{0.5}O₁₄) including Al_{Ga}-substituted variants, and rare-earth oxyborates [ReCa₄O(BO₃), where Re = a rare earth material]. The relevant room temperature d coefficients are generally less than 10 pC N⁻¹ (cf. PZT, 200 pC N⁻¹–700 pC N⁻¹) with coupling coefficients $k < 0.2$ (cf. PZT, 0.5–0.7) although in oxyborates, these may be as high as 15 pC N⁻¹ and 0.3, respectively. While the relatively low piezoelectric coupling is unsuitable for active applications, the permittivities in these materials are also low; hence, the g coefficients are attractive for passive sensing applications, for example, in aerospace vibration monitoring. However, the low permittivity also means that the voltage response can be diluted by circuit capacitance, confirming that, if available with sufficient temperature stability, higher k materials would be preferred.

Many Aurivillius-type and other layer-structure ferroelectrics exhibit high Curie temperatures, with values of over 800 °C and 900 °C having been recorded for CaBi₄Ti₄O₁₅ and Bi₃TiNbO₉, respectively. The d coefficients of these materials are typically less than 20 pC N⁻¹, with k values of less than 0.1. Contrary to the trends

suggested by the Landau–Devonshire thermodynamics, the d coefficients of these materials are surprisingly independent of temperature up to the depoling temperature.³⁰ This is possibly one of the reasons why modified $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($T_C = 655^\circ\text{C}$, $d_{33} = 20\text{ pC N}^{-1}$) is employed commercially in a number of applications.

Another non-perovskite ferroelectric employed commercially is tungsten bronze, lead metaniobate PbNb_2O_6 , with $T_C \approx 570^\circ\text{C}$. This material is attractive more for its low electromechanical Q (≈ 20) and high anisotropy (d_{33}/d_{31} ratio), useful in high-bandwidth ultrasound transducers, than for its moderately high T_C as its large thermal expansion at temperatures above 300°C can be difficult to manage.

C. Bi-based perovskites

1. Binary solid solutions

It is understandable that engineers, when intending to extend the operation of their PZT-based devices to higher temperature, would prefer piezoelectric coupling similar to that achieved in PZT rather than the values exhibited by the high temperature piezoelectrics discussed above. Similar to much of the work on lead-free materials, an obvious strategy for achieving PZT-like performance is to mimic the morphotropic phase boundary seen in PZT. In the case of targeting higher T_C , the most direct approach would be to replace one of the PZT end-members with a higher Curie temperature alternative. Given the relative scarcity of tetragonal perovskites, the most common approach has been to replace PbZrO_3 . For example, Eitel *et al.*³¹ explored a large number of PbTiO_3 solid solutions, revealing a correlation between T_C at the resulting MPB and the cation radius of the rhombohedral end-member. More importantly, they showed that the relatively large ionic radius of the Bi^{3+} ion produced materials with MPB Curie temperatures up to 600°C , in $\text{BiMeO}_3\text{--PbTiO}_3$, where $\text{Me} = \text{Sc}^{3+}$, In^{3+} , and Yb^{3+} . The most accommodating of these materials, $0.36\text{ BiScO}_3\text{--}0.64\text{ PbTiO}_3$, has $d_{33} = 460\text{ pC N}^{-1}$ with $T_C = 450^\circ\text{C}$. Although materials based on this composition are commercially available with operating temperatures up to 350°C , the cost of the Sc_2O_3 precursor can be a challenge in an industry based on PZT.

The solid solution $\text{BiFeO}_3\text{--PbTiO}_3$ appears to buck the trend discovered by Eitel³¹ as the small Fe^{3+} radius compared to Sc^{3+} would suggest a much lower T_C than that of $\text{BiScO}_3\text{--PbTiO}_3$; however, in reality, the T_C for the MPB composition at $0.7\text{ BiFeO}_3\text{--}0.3\text{ PbTiO}_3$ is 635°C .³² Perhaps more remarkable is that, unlike most solid solutions of PbTiO_3 , in which the relatively high spontaneous strain of 6% in pure PbTiO_3 is reduced through solid-solution formation, in $\text{BiFeO}_3\text{--PbTiO}_3$, the spontaneous strain increases with increasing BiFeO_3 content such that for compositions just to the PbTiO_3 -rich side of the MPB, the spontaneous strain peaks at almost 20%.³³ This unprecedentedly large strain, while promising large spontaneous polarization and corresponding intrinsic piezoelectric properties, also presents many difficulties for ceramic preparation and utilization. The large spontaneous strain can promote disintegration of the ceramic following sintering; however, careful processing, in terms of particle size and the sintering temperature profile, can result in materials, which do not disintegrate, but rather counter-intuitively, due to their mixed phase nature, they exhibit anomalously high strength and toughness.^{34,35} However, the piezoelectric properties are characterized as being very hard compared to PZT due to the difficulty of switching ferroelastic domains with such a

high spontaneous strain. In addition, the conductivity reduces the electrical time constant to impractical levels. Doping with a number of elements, particularly donor dopants such as La^{3+} , can simultaneously reduce both the conductivity and spontaneous strain to produce a softer piezoelectric with more practical time constants, albeit at the expense of reducing T_C to a temperature similar to that of PZT.³⁶

Tetragonal ferroelectric perovskites other than PbTiO_3 have been investigated in solid solution with BiFeO_3 . The most obvious candidate is $\text{BiFeO}_3\text{--BaTiO}_3$; however, unlike $\text{BiFeO}_3\text{--PbTiO}_3$, its phase diagram does not exhibit a strongly tetragonal phase. The Bi-rich tetragonal phase transforms to “cubic” at $<10\%$ BiFeO_3 , with a second phase boundary to the Bi-rich rhombohedral phase at around 65% BiFeO_3 . The addition of BaTiO_3 to BiFeO_3 also results in a decline in T_C .³⁷ Although some authors have identified the non-rhombohedral phase as tetragonal, most suggest that despite it being crystallographically cubic or “pseudo-cubic,” it appears to exhibit a substantial high-field piezoelectric effect close to the boundary with the rhombohedral phase, which can be attributed to a field-induced transition from a non-polar to a polar state.³⁸ However, through combinations of very specific thermal processing³⁹ and doping,⁴⁰ materials with useful combinations of T_C ($\sim 450^\circ\text{C}$) and d_{33} (240 pC N^{-1}) can be produced.

The loss of long-range polar order on alloying BiFeO_3 with a tetragonal perovskite appears to be the rule, to which PbTiO_3 is one of the few exceptions. A similar behavior to $\text{BiFeO}_3\text{--BaTiO}_3$ is observed in the $\text{BiFeO}_3\text{--}(\text{K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ solid solution, in which a relaxor phase results.⁴¹ While relaxors are perennially of scientific interest,⁴² their properties, derived from the dynamics of domains of short range polar order, diverge from conventional piezoelectricity. The large strains that can be generated are often a mixture of electrostriction and field-induced spontaneous strain, while the weak field piezoelectric effect tends to zero or is rather small. Hence, they are generally not preferred for conventional piezoelectric applications such as ultrasound transducers. For clarity, it should be pointed out that piezoelectric relaxor- PbTiO_3 single crystals referred to earlier⁹ are actually ferroelectric in their behavior; the relaxor in their descriptor refers mainly to the classification of the non- PbTiO_3 end-member.

Both $\text{BiFeO}_3\text{--PbTiO}_3$ and $\text{BiFeO}_3\text{--BaTiO}_3$ type solid solutions exhibit complex crystallographic, microstructural, and electromechanical behavior near the putative MPBs, for which the origins, in the magnitude of tetragonal spontaneous strain, are almost diametrically opposed. Both of these simple binaries present challenges in terms of optimization for applications or industrial scale-up.

2. Ternary systems

On the one hand, the MPB composition in $\text{BiFeO}_3\text{--PbTiO}_3$ offers a high Curie temperature (635°C), but with exceptionally hard properties due to the large spontaneous strain, with a concern that conductivity due to $\text{Fe}^{2+}/\text{Fe}^{3+}$ mediated hopping is too high for high temperature operation. On the other hand, other tetragonal end-members result in the breakdown of long-range order, a reduction in T_C , and the onset of relaxor behavior.⁴³ As a general rule, increasing the number of cations in a solid solution tends to further undermine polar coherence and deepen the relaxor nature; however, incorporation of PbTiO_3 in nano-polar systems tends to overcome the loss of coherence and favors the formation of

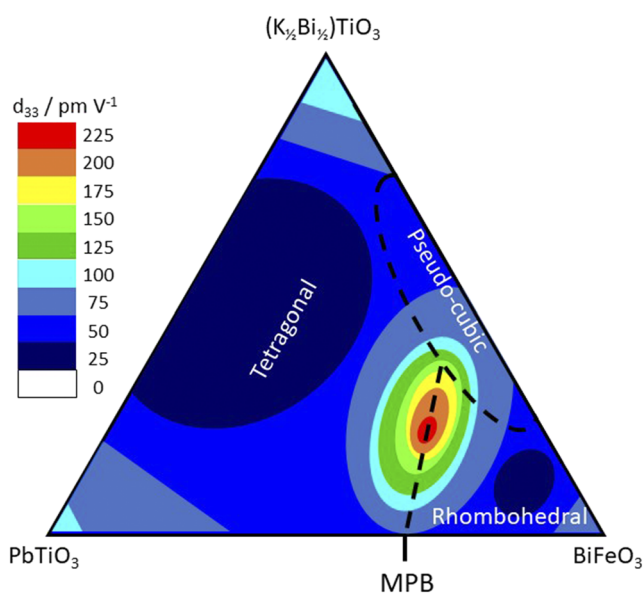


FIG. 1. Schematic of the $\text{BiFeO}_3\text{-PbTiO}_3\text{-(K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ phase diagram showing the variation of the room temperature piezoelectric charge coefficient with composition, based on the experimental data of Bennett.⁴⁴ Dashed lines show inferred phase boundaries.

long-range polar order. This can be clearly seen in the example of $\text{BiFeO}_3\text{-PbTiO}_3\text{-(K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ (Fig. 1),⁴⁴ in which the largest weak-field d_{33} is located virtually mid-way between the $\text{BiFeO}_3\text{-PbTiO}_3$ MPB composition and the pseudo-cubic region of $\text{BiFeO}_3\text{-(K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$.⁴⁵ Similar performance has recently been reported in the $\text{BiFeO}_3\text{-PbTiO}_3\text{-BaTiO}_3$ system,⁴⁶ in which BaTiO_3 plays the same role as $(\text{K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$. Compared to the MPB composition in the $\text{BiFeO}_3\text{-PbTiO}_3$ binary, the ternary sweet-spot compositions exhibit reduced conductivity, reduced tetragonality,⁴⁷ reduced coercive field, and an increase in domain wall contributions to the polar properties.⁴⁸ While there is still an inverse relationship between d_{33} and T_C , $\text{BiFeO}_3\text{-PbTiO}_3\text{-(K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ compositions with $T_C \approx 510^\circ\text{C}$, $T_d \approx 490^\circ\text{C}$, and $d_{33}(20^\circ\text{C}) > 150 \text{ pm V}^{-1}$, consistent with $d_{33}(480^\circ\text{C}) > 300 \text{ pm V}^{-1}$, are achievable. Further extension of the operating temperature range to 580°C through an increase in the Curie temperature to 680°C has been achieved through careful optimization of the process parameters.⁴⁹ Such properties represent a major step forward compared to the previous state of the art properties, and over the last 5 years, they have been commercialized in a range of applications.

IV. APPLICATIONS

The combination of the relatively high d_{33} of the $\text{BiFeO}_3\text{-PbTiO}_3\text{-(K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ material and an operating temperature that can be extended up to almost 600°C has created a step change in a number of areas of application. Compared to non-ferroelectrics, and non-perovskites, the high coupling allows high temperature active operation (converse mode), rather than only using the material for sensing (direct mode).

For example, a significant impact has been made in the field of ultrasonic devices for plant inspection. Time-of-flight ultrasound, using piezoelectric transducers, is the main method for inspecting industrial plants for cracks and corrosion at room temperature.⁵⁰ However, until the introduction of new materials, ultrasonic inspection at high operating temperatures ($200^\circ\text{C}\text{-}580^\circ\text{C}$) had proved to be challenging as piezoelectric materials with sufficiently high coupling over that temperature range did not previously exist. Consequently, in the energy, nuclear, and oil and gas industries, it is common practice to shut-down plants to allow them to cool and to allow both scheduled and unplanned ultrasound inspections to take place. Such closures can cost up to $\$1 \text{ m/day}$ in the nuclear industry, for example, and run to $\$100 \text{ m}'\text{s p.a.}$ in unscheduled outage costs, emergency repairs, and insurance and legal costs. The recent availability of transducers for continuous use up to 580°C has, therefore, been transforming inspection practice, allowing not only inspections for corrosion and cracking to take place without interruption to normal operations but also allowing transducers to be permanently installed at critical areas of plants for continuous monitoring, bringing the benefits of reduced inspection costs and increased safety and savings in plant maintenance and asset replacement.⁵¹

Structural health monitoring systems for aeroengines are also under development, based on the commonly used endoscope concept, but incorporating temperature resistant materials to allow high temperature deployment. This will allow the detection of cracks that are only apparent in the elevated temperature range immediately post-flight. In addition, ultrasonic position monitoring systems for aeroengines have been demonstrated, offering direct feedback on the operational status of mechanical components such as fuel valves in-flight.

In terms of process control in high temperature plants, both time of flight and Doppler devices, with extended operating temperatures, are operational for the non-invasive measurement of liquid and gaseous flow velocities, providing multiple benefits in plant management.

A corollary of the ability of high T_C materials to withstand high operating temperatures is the ability to withstand high stresses without de-poling. Due to this enhanced capability, materials in the $\text{BiFeO}_3\text{-PbTiO}_3\text{-(K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ system now find applications in combined extreme pressure and temperature environments such as exhaust gas metering transducers, for example, with a combined stress and temperature withstanding ability of $>100 \text{ MPa}$ at $>400^\circ\text{C}$.

High temperature actuation has always proved more challenging than sensing as the frequency range tends to be lower and more susceptible to high power losses due to electrical conductivity. However, the new BiFeO_3 -based materials have sufficiently large d coefficients and acceptably low conductivity to act as actuators with relatively high strain (d^*) coefficients $>200 \text{ pm V}^{-1}$ at 400°C .⁵² Such properties have proved to provide sufficient energy coupling for the efficient atomization of molten polymers, metals, and glasses.

Perhaps somewhat unexpected is the fact that these materials also exhibit significantly greater fracture strength and fracture toughness than PZT, evidenced as 2.5 times greater strain to failure.⁵³ This is thought to be a combination of the larger intrinsic strength of Bi-based compounds than PZT and a transformation toughening contribution due to the large spontaneous strain of the tetragonal component of the MPB compositions. Hence, micro-engineered actuators can be designed with much higher

dimensional aspect ratios than with PZT, and as it has also been shown with BiScO₃-PbTiO₃,⁵⁴ high T_C materials used in energy harvesting cantilevers can withstand higher accelerations with larger proof masses, resulting in >5 times the power density of PZT devices.

As the new materials become more widely known, new applications are emerging regularly. Unfortunately, many of these are proprietary and still confidential. Nevertheless, the impact of material research is proving to be beyond initial expectations, with many of the new applications only becoming evident once the capabilities of the material are established.

V. CONCLUSIONS

BiFeO₃-based ceramics are now fulfilling the promise of significantly widening the operational window for high-activity piezoelectric materials that has been virtually unchanged for almost 60 years. They provide both sensing and actuation functions up to 400 °C and with excellent ultrasound performance up to almost 600 °C. The larger coupling coefficients and manufacturing flexibility compared to non-ferroelectric single crystals also provide them with advantages for vibration monitoring over this same temperature range. For low stress applications, they cannot compete with PZT below 300 °C, but their higher de-poling stress means that they are the material of choice for applications requiring high stress operation (>250 MPa) at modest temperatures or combinations of stress and temperature up to 100 MPa at 400 °C. Their high fracture strength and strain-to-failure encourage a relaxation of design rules for high aspect ratio component parts for micro-actuation and energy harvesting.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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