TOPICAL REVIEW

Progress in engineering high strain lead-free piezoelectric ceramics

Serhiy O Leontsev and Richard E Eitel

Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, USA
E-mail: reitel@engr.uky.edu

Received 2 April 2010
Accepted for publication 5 July 2010
Published 10 September 2010
Online at stacks.iop.org/STAM/11/044302

Abstract

Environmental concerns are strongly driving the need to replace the lead-based piezoelectric materials currently employed as multilayer actuators. The current review describes both compositional and structural engineering approaches to achieve enhanced piezoelectric properties in lead-free materials. The review of the compositional engineering approach focuses on compositional tuning of the properties and phase behavior in three promising families of lead-free perovskite ferroelectrics: the titanate, alkaline niobate and bismuth perovskites and their solid solutions. The ‘structural engineering’ approaches focus instead on optimization of microstructural features including grain size, grain orientation or texture, ferroelectric domain size and electrical bias field as potential paths to induce large piezoelectric properties in lead-free piezoceramics. It is suggested that a combination of both compositional and novel structural engineering approaches will be required in order to realize viable lead-free alternatives to current lead-based materials for piezoelectric actuator applications.

Keywords: lead-free, ferroelectric ceramics, piezoelectricity, morphotropic phase boundary, polymorphic phase transformation, domain engineering, templated grain growth, grain size effect

1. Introduction

Piezoelectric ceramic materials are widely used in modern industry to transform electrical signals into mechanical strain and vice versa; this dual nature enables piezoelectric materials to be used in electromechanical systems as both sensors and actuators [1]. Current applications of piezoelectric devices extend to automotive fuel injection, accelerometers, piezoelectric transformers and motors, vibration control, micropositioning systems, ultrasound sensors and generators, inkjet printers and many more [2–5]. In the particular case of piezoelectric actuator applications, the piezoelectric strain coefficient ($d_{33}$) and its temperature dependence are the critical performance metrics.

Currently, piezoceramic actuator materials in commercial use are based on lead titanate zirconate (PbZrO$_3$–PbTiO$_3$ or PZT). PZT possesses superior dielectric and piezoelectric properties arising from the existence of a morphotropic phase boundary (MPB) between tetragonal and rhombohedral phases at $\sim$48 mol% PbTiO$_3$ content [5–7]. Piezoelectric coefficients ($d_{33}$) as high as 779 pC N$^{-1}$ have been reported for modified PZT [8] with Curie temperatures ($T_c$) in the range 300–400 $^\circ$C. The large properties induced by the MPB and high ferroelectric Curie temperature result in excellent thermal stability in PZT and allow use at operational temperatures $\sim$175 $^\circ$C or following temperature transients approaching $T_c$. Additionally, a wide variety of dopants can be used to manufacture a range of ‘hard’ and ‘soft’ PZT piezoelectrics tuned for specific applications [5].

The commercial manufacture and application of lead titanate zirconate have recently become a concern from the viewpoint of health and environmental protection. The
evaporation of lead during high-temperature sintering and improper disposal of lead-based materials represent serious health hazards and are now strictly regulated. In the last decade, legislation governing the use of lead containing compounds has been enforced in the EU and the State of California including the draft Directives on Waste from Electrical and Electronic Equipment (WEEE), Restriction of Hazardous Substances (RoHS) and End-of-Life Vehicles (ELV) [9–12]. Therefore, the need to reduce environmental contamination by lead-based substances has created the current drive to develop alternative lead-free piezoelectric materials. Despite tremendous recent progress, currently no lead-free materials possess both the high piezoelectric strain coefficients ($d_{ij}$) and thermal stability required to provide a viable replacement for PZT-based materials for piezoelectric actuator applications [13–15].

2. Engineering approach to high-performance lead-free piezoelectrics

Traditionally, enhancement of the electromechanical response in piezoelectric materials is achieved by compositional engineering. Following this approach the composition of a material or solid-solution is optimized to bring the material into proximity with a structural instability such as polymorphic phase transition (PPT) or morphotropic phase boundary (MPB) [5]. Hypothetical phase diagrams used for compositional engineering of both PPT- and MPB-based piezoceramics systems and the resulting temperature dependence of the piezoelectric response are illustrated in figure 1. In both cases, improved piezoelectric properties result from a combination of (i) a ‘softening’ the crystal lattice due to the coexistence of two phases with equivalent free energies and (ii) increased alignment of ferroelectric domains following poling enabled by the large number of equivalent polarization directions from the different symmetries of the two phases. As illustrated in figure 1(c), MPB-based piezocermics typically exhibit relatively flat temperature dependence of the poled piezoelectric properties and broad usage temperatures approaching $\sim 1/2T_C$. Conversely, PPT-based piezocermics generally exhibit large temperature dependence of the piezoelectric coefficient and rapid degradation of poled piezoelectric coefficient (due to partial depoling) subsequent to temperature excursions close to the PPT temperature. Recently, the depolarization temperature ($T_d$) has been proposed to describe the temperature at which a poled ferroelectric material completely or partially depolarizes, as determined from pyroelectric measurements [16]. This temperature typically coincides with the ferroelectric Curie temperature. However, in materials exhibiting one or more polymorphic phase transitions below the ferroelectric Curie temperature but above room temperature, $T_d$ refers to the temperature of the lowest of these phase transitions.

In contrast to compositional engineering approaches, the 'structurally engineered materials' approach focuses on controlling the micro and/or nanoscale structure of a piezoelectric material. Significant enhancements of electromechanical properties have been achieved utilizing various structural engineering techniques including; templated grain growth [17, 18], grain size optimization [19] and domain engineering [20–22]. The resulting enhancement of piezoelectric properties using several structural engineering approaches is illustrated in figure 2. The above methods have been applied to a wide variety of existing piezoelectric materials including: bulk and single crystal BaTiO$_3$, PZT ceramics and bulk and single crystal Pb(Mg$_{1-x}$Nb$_x$)TiO$_3$–PbTiO$_3$. These methods represent an important future path for engineering practical high-performance lead-free piezoelectrics.
realizing viable lead-free piezoelectric ceramics for actuator applications is discussed by comparing reported piezoelectric coefficients and depolarization temperatures of both lead-free and lead-based piezoelectric ceramic (section 6).

3. Titanate perovskites

Perovskite ferroelectrics in which the ferroelectric cation is the B-site Ti$^{4+}$ ion make up a large fraction of the materials under consideration for lead-free piezoelectrics. Published piezoelectric coefficients and relevant phase transition temperatures for the titanate perovskites and their solid solutions are summarized in table 1.

3.1. Barium titanate

Barium titanate BaTiO$_3$ is the prototype polymorphic phase transition (PPT)-based high-performance piezoceramic material. The discovery of the process for poling barium titanate led to development of the first polycrystalline piezoelectric ceramics [23, 24]. The piezoelectric coefficient $d_{33}$ of pure BaTiO$_3$ fabricated by conventional solid state processing is approximately 190 pC N$^{-1}$ [25]. Prior to the discovery of PZT-based materials, BaTiO$_3$ was used in naval sonar applications and phonograph needles; however, widespread commercial application of BaTiO$_3$ for piezoelectric actuators remains limited by its low Curie temperature ($T_C = 120^\circ$C) [5] which severely constrains the operational (or transient exposure) temperature for BaTiO$_3$ materials.

Recently, structural engineering approaches by several groups have led to significantly improved piezoelectric response in BaTiO$_3$. Introduction of fine-scale ferroelectric domains into barium titanate ceramics prepared from nano-scale particles and densified by microwave sintering results in a high $d_{33}$ value of 350 pC N$^{-1}$ [26–28]. In other work, a piezoelectric coefficient of 460 pCN$^{-1}$ is achieved in high-quality hydrothermally synthesized BaTiO$_3$ powders and an optimized conventional sintering process, resulting in fine grain ceramics, with grain sizes on order of 1–2 $\mu$m [29, 30]. A separate report also describes the tendency of the piezoelectric coefficient to increase with decreasing domain size [19]. This increased $d_{33}$, in small grain and small domain size randomly oriented ceramics, has also been combined with the templated grain growth technique and further enhancement in the piezoelectric coefficient reported. A $d_{33}$ value of 788 pC N$^{-1}$ was reported in [110] grain oriented BaTiO$_3$ ceramics with submicron domain size [21]. These findings clearly demonstrate the large piezoelectric response achievable in optimally prepared ceramics (up to 460 pC N$^{-1}$ in hydrothermal BaTiO$_3$) and that structural engineering is a key concept in achieving enhanced piezoelectric properties in lead-free piezoceramics (up to ~800 pC N$^{-1}$ in grain-oriented BaTiO$_3$).

3.2. Bismuth potassium titanate

Bismuth potassium titanate (Bi$_{1/2}$K$_{1/2}$TiO$_3$ (BKT) is another common lead-free ferroelectric ceramic material.
Table 1. Room-temperature piezoelectric coefficients \( (d_{33}) \), depolarization temperature \( (T_d) \), and Curie temperatures \( (T_C) \) for the titanate perovskites. Notes: Where available the measurement method used for determining the piezoelectric coefficient is indicated: * Refers to a Berlincourt-type meter and # to the IEEE resonance method. The type of polymorphic phase transition occurring at \( T_d \) is indicated as follows: O–T, orthorhombic-tetragonal; PC, transformation to a pseudocubic phase; AFE, antiferroelectric phase transformation, or *-unknown. Other abbreviations: BKT (\( \text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3 \)) and BNT (\( \text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3 \)).

| Material | \( d_{33} \) (pC N\(^{-1}\)) | \( T_{PPT} \) (°C) | \( T_C \) (°C) | Comment, reference |
|----------|-------------------------------|-------------------|----------------|----------------------------------|
| BaTiO\(_3\) | 190* | 0 | 120 | [5] |
| BaTiO\(_3\) | 350* | 0 | 120 | [26] |
| BaTiO\(_3\) | 460* | 24 | 126 | [29] |
| BaTiO\(_3\) | 788* | 0 | 120 | [21] |
| BKT | 70# | PC | 410 | [34] |
| BKT | 82# | PC | 410 | Hot-pressed |
| BKT–Bi | 100# | PC | 280 | [36] |
| BaTiO\(_3\)–BKT20 + Mn | 76# | none | 230 | [15] |
| BaTiO\(_3\)–BKT5 + Mn | 100# | none | 168 | [15] |
| BNT–BaTiO\(_3\) | 155* | AFE | 85 | 288 | [51] |
| BNT–BaTiO\(_3\) + Li | 208 | AFE | 260 | [54] |
| BNT–BKT | 150# | PC | 210 | 320 | [60] |
| BNT–BKT | 144* | PC | 174 | 330 | [58] |
| BNT–BKT | 157# | PC | 162 | 280 | [59] |
| BNT–BKT–BaTiO\(_3\) | 170* | AFE | 197 | 262 | [66] |
| BNT–BKT–BaTiO\(_3\) | 135# | AFE | 210 | 290 | [67] |
| BNT–BKT–BaTiO\(_3\) + Li | 205* | AFE | N/A | [68] |

(\( \text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3 \)) was originally fabricated by Popper et al.\(^{[31]}\) in 1957 and its ferroelectricity including Curie temperature of 370 °C was confirmed later by Buhrer\(^{[32]}\). At room temperature, (\( \text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3 \)) has the perovskite structure with tetragonal symmetry and exhibits a second phase transition to a pseudocubic structure at around 300 °C. (\( \text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3 \)) ceramics are difficult to sinter\(^{[33]}\), however, high densities of 97% of theoretical can be achieved by hot pressing methods yielding piezoelectric \( d_{33} \) coefficients close to 70 pC N\(^{-1}\)\(^{[34]}\). Hot pressed (\( \text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3 \)) shows
increased $T_C$ of 410–435°C and the temperature of the second phase transition increases to 315–340°C. Slightly improved piezoelectric properties in (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ ceramics are obtained using an optimized poling procedure resulting in a $d_{33}$ of 82 pC N$^{-1}$ [35]. Alternatively, doping with bismuth and using sintering aids has further increased the $d_{33}$ value to 100 pC N$^{-1}$ [36].

3.3. Bismuth sodium titanate

Bismuth sodium titanate, (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ (BNT), first reported by Smolenkii et al in 1960, is another important lead-free piezoelectric material [37]. (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ was found to be a perovskite-type ferroelectric at room temperature and exhibits relaxor ferroelectric behavior. A diffuse phase transformation in the temperature range 200–320°C is observed in (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ corresponding to a transition from rhombohedral to tetragonal symmetry [38–41]. This transition is rather complex and it is believed that it takes place through an intermediate orthorhombic antiferroelectric phase [42]. The preparation of dense (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ ceramics is difficult, requiring sintering temperatures above 1200°C, which results in significant loss of bismuth. High leakage currents and high coercive field negatively impact the poling process and polarization saturation is difficult to achieve in conventionally fabricated (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ samples. However, dense ceramics have been obtained using excess Bi or hot pressing sintering methods, yielding samples with saturated polarization loops [43]. (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ ceramics fabricated by these latter techniques have piezoelectric $d_{33}$ coefficients 94–98 pC N$^{-1}$ and a depolarization temperature of 200°C [37, 42, 43].

3.4. Bismuth potassium titanate–barium titanate solid solution

Both barium titanate (BaTiO$_3$) and bismuth potassium titanate ((Bi$_{1/2}$K$_{1/2}$)TiO$_3$) are tetragonal ferroelectric materials with Curie temperatures of 120 and 370°C, respectively. The binary system (Bi$_{1/2}$K$_{1/2}$)TiO$_3$–BaTiO$_3$ (BKT–BT) has been investigated in order to obtain a compound with enhanced piezoelectric properties and higher $T_C$ than pure BaTiO$_3$. The solid solution $x$(Bi$_{1/2}$K$_{1/2}$)TiO$_3$–(1–$x$)BaTiO$_3$ is single phase ferroelectric perovskite over the complete compositional range and shows close to linear dependence of the Curie temperature on (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ concentration, as shown in figure 3 [15]. In compositions above $x = 60$ mol\% (Bi$_{1/2}$K$_{1/2}$)TiO$_3$, a second transition from tetragonal to an intermediate pseudocubic phase is observed at around 300°C and remains nearly independent of (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ concentration. Values of the piezoelectric $d_{33}$ coefficient do not change significantly with composition and are in the range 60–70 pC N$^{-1}$. The highest $d_{33}$ of 100 pC N$^{-1}$ is obtained for $x = 5$ mol\% (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ with the addition of manganese, however, this composition has a relatively low Curie temperature of 168°C. Compositions with $x > 60$ mol\% (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ show good thermal stability of the coupling coefficient up to their depolarization temperature, $T_d ∼ 250°C$, and are considered attractive for piezoelectric applications even with their low $d_{33}$’s ∼ 70 pC N$^{-1}$. Structural engineering in (Bi$_{1/2}$K$_{1/2}$)TiO$_3$–BaTiO$_3$ leads to a significantly improved $d_{33}$ value of 121 pC N$^{-1}$, for $x = 10$ mol\% (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ textured using the templated grain growth technique [44, 45].

3.5. Bismuth sodium titanate–barium titanate solid solution

It might be expected that the solid solution of the rhombohedral ferroelectric bismuth sodium titanate (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ and a tetragonal material such as barium titanate would exhibit a rhombohedral–tetragonal morphotropic phase boundary (MPB) as in the prototype PZT system. Subsequently this binary system (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$–BaTiO$_3$ (BNT–BT) was investigated by Takenaka et al [46, 47] and the existence of an MPB was confirmed at around 6–7 mol\% BaTiO$_3$, as illustrated in figure 4. Enhanced dielectric constant, electromechanical coupling coefficient, and piezoelectric properties ($d_{33} = 125$ pC N$^{-1}$), compared to unmodified BNT ($d_{33} = 64$ pC N$^{-1}$), were observed at the MPB [48, 49]. Piezoelectric coefficients in the range 122–176 pC N$^{-1}$ at the MPB have been reported by various researchers [50–53]; $d_{33}$ values of 208 pC N$^{-1}$ were achieved in lithium-modified (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$–BaTiO$_3$ [54, 55]. Whereas the MPB composition for (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$–BaTiO$_3$ has a relatively high $T_C$ of 288°C, a low depolarization temperature ($T_d$) of 150°C has been reported. By analogy to the (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ end member, the low $T_d$ arises owing to a polymorphic phase transformation to an antiferroelectric (AFE) phase, as substantiated by high-temperature dielectric and polarization hysteresis measurements [46].

3.6. Bismuth sodium titanate–bismuth potassium titanate solid solution

The solid solution of bismuth sodium titanate, (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ (BNT), and bismuth potassium titanate, (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ (BKT), was synthesized by Elkechai et al in 1996 [56] and an increase in piezoelectric
properties was observed in this system close to the rhombohedral to tetragonal morphotropic phase boundary, shown in figure 5. The existence of an MPB between \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\) and \((\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\) in the compositional range 16–20 mol% \((\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\) was later substantiated by Sasaki et al. [57] based on structural studies indicating coexistence of rhombohedral and tetragonal phases as well as the corresponding compositionally dependent peaks in the dielectric, piezoelectric and electromechanical coefficients. More recent studies [58–63] confirm high piezoelectric properties \((d_{33})\) in the range 140–192 pC N\(^{-1}\)) at the MPB composition. The Curie temperature of the MPB \((T_C = 280–300°C)\) is higher than that of pure \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\) as expected, however, the depolarization temperature (due to a polymorphic phase transformation to the intermediate pseudocubic phase) is quite low reaching a minimum \((T_d = 140°C)\) at the MPB.

3.7. Barium titanate–bismuth sodium titanate–bismuth potassium titanate ternary solid solution

The ternary \(\text{BaTiO}_3–(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3–(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\) (BT–BNT–BKT) solid solution (phase diagram shown in figure 6) has also been widely investigated owing to relatively large Curie temperatures and high piezoelectric properties. BT–BNT–BKT exhibits a tetragonal–rhombohedral MPB and while maintaining piezoelectric properties similar to its end members. Reported values of the piezoelectric \(d_{33}\) coefficient are in the range 135–191 pC N\(^{-1}\)) and are inversely proportional to the observed depolarization temperature, which is prohibitively low \((T_d \sim 110°C)\) at the MPB [64–66]. For compositions with a more reasonable depolarization temperature \((T_d = 197°C)\) a maximum \(d_{33}\) of 135 pC N\(^{-1}\)) was obtained [67]. Further enhanced performance was found in Li-modified BT–BNT–BKT, exhibiting a \(d_{33}\) of 205 pC N\(^{-1}\), with a depolarization temperature \(T_d = 210°C\) [68].

4. Alkaline niobates

The alkaline niobates and their solid solutions are another interesting family of lead-free perovskites. Significant recent experimental efforts in these materials have been undertaken largely following Saito et al.’s 2004 Nature paper and the accompanying editorial ‘Lead Free at Last’ [13, 69]. While exhibiting high piezoelectric coefficients, particularly in structurally engineered ceramics these materials are still limited in application by low depolarization temperatures arising from an orthorhombic to tetragonal (O–T) PPT near room temperature. Published room-temperature piezoelectric coefficients and phase transformation temperatures for the alkaline niobates and solid solutions are compiled in table 2.

4.1. Potassium niobate

In 1951, Matthias and Remeika [70] discovered ferroelectricity in \(\text{KNbO}_3\) reporting both its Curie temperature \((T_C = 435°C)\) and a second transition temperature at around 225°C. Further investigations revealed a sequence of phase transformations similar to those observed in \(\text{BaTiO}_3\) (rhombohedral–orthorhombic–tetragonal–cubic) occurring at ~10, 220 and 420°C, respectively [71]. Pure \(\text{KNbO}_3\) ceramics are difficult to fabricate [5], however, single crystals

---

**Figure 4.** Phase diagram for the \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3–\text{BaTiO}_3\) solid solution (after [46]).

**Figure 5.** Phase diagram for the \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3–(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\) solid solution (after [56, 59, 62]).

**Figure 6.** Ternary phase diagram for the \(\text{BaTiO}_3–(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3–(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\) solid solution (after [65, 67]).
Table 2. Room-temperature piezoelectric coefficients ($d_{33}$), depolarization temperature ($T_D$) and Curie temperatures ($T_C$) for the alkaline niobate perovskites. For all cases report the $T_D$ is associated with an orthorhombic–tetragonal PPT (O–T). Notes: Where available the measurement method used for determining the piezoelectric coefficient is indicated: * refers to a Berlincourt-type meter and # to the IEEE resonance method. O–T: orthorhombic–tetragonal.

| Material                  | $d_{33}$ (pC N$^{-1}$) | $T_{DPT}$ (°C) | $T_C$ (°C) | Comment, reference |
|---------------------------|------------------------|----------------|------------|--------------------|
| KNbO$_3$                  | 97                     | 220            | 435        | [76]               |
| (K,Na)NbO$_3$             | 80                     | 195            | 420        | [82]               |
| (K,Na)NbO$_3$             | 127                    | 195            | 420        | [90]               |
| (K,Na)NbO$_3$ + Sb        | 218*                   | 170            | 352        | [119]              |
| (K,Na)NbO$_3$ + Ag        | 186*                   | 20             | 355        | [120]              |
| (K,Na)NbO$_3$ + Li        | 240*                   | 50             | 460        | [121]              |
| (K,Na)NbO$_3$ + Li,Ta     | 190*                   | 50             | 310        | [121]              |
| (K,Na)NbO$_3$ + Li,Ta     | 230*                   | 35             | 323        | [99]               |
| (K,Na)NbO$_3$ + Li,Ta     | 262*                   | 27             | 325        | [122]              |
| (K,Na)NbO$_3$ + SrTiO$_3$ | 200*                   | 55             | 277        | [123]              |
| (K,Na)NbO$_3$ + LiTaO$_3$ | 200*                   | 70             | 430        | [95]               |
| (K,Na)NbO$_3$ + LiNbO$_3$ | 235*                   | 35             | 452        | [124]              |
| (K,Na)NbO$_3$ + LiSbO$_3$ | 265#                   | 35             | 368        | [102]              |
| (K,Na)NbO$_3$ + Li,Sn,Sb  | 142*                   | 115            | 353        | [125]              |
| (K,Na)NbO$_3$ + Li,Sb,Ta  | 400*                   | 20             | 230        | [126]              |
| (K,Na)NbO$_3$ + Li,Sb,Ta,LF4 | 300*                | 25             | 253        | [13, 103]          |
| (K,Na)NbO$_3$ + Li,Sb,Ta,LF4T | 416*               | 25             | 253        | [13, 103]          |
| (K,Na)NbO$_3$ + LiSbO$_3$ + CaTiO$_3$ | 210*            | 43             | 296        | [105]             | O$_2$ sintering
| (K,Na)NbO$_3$ + Li,Sb,Ta  | 370*                   | 50             | 270        | [127]              |
| (K,Na)NbO$_3$ + Sn,LiTaO$_3$ | 321*               | 50             | 315        | [128]              |
| (K,Na)NbO$_3$ + Li,Ag     | 220*                   | 145            | 476        | [129]              |
| (K,Na)NbO$_3$ + AgSbO$_3$ | 192*                   | 145            | 348        | [130]              |

have been produced and interesting nonlinear electro-optic properties and piezoelectric coefficients along certain crystallographic directions have been reported [72–74]. High coupling coefficients ($k_T = 0.69$) and excellent temperature stability up to 160 °C make KNbO$_3$ single crystals attractive for ultrasonic and acoustic wave transducer applications, however, other uses of KNbO$_3$’s piezoelectric properties are limited [75]. Recent studies on bulk KNbO$_3$ ceramics
report piezoelectric properties with a $d_{33}$ coefficient of 97 pC N$^{-1}$ [76] and large shear-mode $d_{15}$ constant of 207 pC N$^{-1}$ [77, 78].

### 4.2. Sodium niobate

The other alkaline niobate end member, sodium niobate NaNbO$_3$, is also an orthorhombic perovskite at room temperature, transforming into the tetragonal phase at 370°C and eventually to cubic above 640°C [79]. At room temperature, NaNbO$_3$ is antiferroelectric and as such exhibits no piezoelectric activity in its pure form [5].

### 4.3. Potassium niobate–sodium niobate solid solution

The potassium niobate–sodium niobate, KNbO$_3$–NaNbO$_3$ (alternatively (K, Na)NbO$_3$ or KNN) solid solution is widely considered as one of the most promising lead-free alternatives to the conventional piezoelectric ceramics. Both end members of the solid solution are orthorhombic at room temperature and early work on the ceramics in this system indicated multiple temperature-induced phase transformations and morphotropic phase boundaries comprising a rather complex phase diagram, shown in figure 7 [80, 81]. Piezoelectric $d_{33}$ coefficients for KNN are reported in the range 80–160 pC N$^{-1}$ and enhanced electromechanical properties observed near the 53 mol% sodium niobate composition [82–85].

Processing of KNN ceramics is problematic owing to the low sintering temperatures required because of the instability of the KNN phase above 1140°C and volatility of the alkali species at high temperatures. This low temperature requirement makes it difficult to obtain ceramics of high sintered density [5, 85]. However, reasonable piezoelectric properties ($d_{33} = 100$ pC N$^{-1}$) of KNN have been achieved by optimizing the conventional sintering process [85]. The incorporation of liquid phase sintering aids ($K_2CuNb_2O_7$, $K_2CuTi_2O_7$, and CuO) [86–88] can result in densities up to 97.5% theoretical. Liquid phase sintering has reduced sintering temperatures to as low as 950°C, and high-field $d_{33}$’s of 180–270 pC N$^{-1}$ have been reported. Densification of KNN ceramics is also significantly improved by hot-pressing, with sintered ceramics reaching ~99% of the theoretical density and the resulting piezoelectric constant nearly twice the value of conventionally sintered KNN [89–91]. Spark plasma sintering has also resulted in high-density KNN ceramics and with enhanced piezoelectric coefficients ($d_{33} = 148$ pC N$^{-1}$) [92–94].

Numerous compositional engineering approaches have been explored to optimize the piezoelectric properties of KNN materials. However, nearly all of these approaches achieve 'enhanced' properties by shifting the orthorhombic–tetragonal polymorphic phase transition temperature ($T_{O-T}$) to slightly above or below room temperature. As discussed above and illustrated in figure 1, this close proximity to a PPT results in significant softening of the piezoelectric properties (large $d_{33}$), however, comes at the cost of large temperature dependence of the piezoelectric response and poor stability of the poled domain state in most modified KNN compositions.

Compositionally engineered KNN systems modified by LiTaO$_3$ and LiSbO$_3$ have been studied the most intensively. KNN in combination with tetragonal LiTaO$_3$ exhibits a morphotropic phase boundary between orthorhombic and tetragonal phases at 4–5 mol% of LiTaO$_3$ accompanied by enhancement of piezoelectric properties; $d_{33}$ coefficients have been reported in the range 200–259 pC N$^{-1}$ [95–99]. The addition of LiSbO$_3$ to pure KNN shifts the orthorhombic to tetragonal polymorphic phase transition temperature down from 200°C to nearly room temperature ($T_{O-T} \sim 35°C$) and increases the room-temperature $d_{33}$ coefficient; reaching a maximum ($d_{33} = 250–265$ pC N$^{-1}$) at approximately 5 mol% of LiSbO$_3$ content [100–102]. In the work of Saito et al. [13], optimization of the KNN by separate lithium, tantalum and antimony additions (specifically (K$_{0.44}$Na$_{0.52}$Li$_{0.04}$)(Nb$_{0.86}$Ta$_{0.10}$Sb$_{0.04}$)O$_3$, the so-called LF4 composition) yielded a further increase of $d_{33}$ to 300 pC N$^{-1}$. In the same work, the properties of the LF4 composition were further enhanced by the reactive template grain growth method, producing $d_{33}$ values as high as 416 pC N$^{-1}$ in (001) oriented ceramics (LF4T) [13]. The observed enhancement of the piezoelectric coefficient was at first attributed to an MBP between orthorhombic and tetragonal phases. However, the authors themselves and more recent studies observed temperature dependence of the electromechanical properties near the room temperature and the existence of the orthorhombic–tetragonal PPT near room temperature in both the LF4 and LF4T compositions [13, 103].

Recently, an alternative modification of the KNN system has been proposed [104, 105]. In this work it is shown that the orthorhombic to tetragonal phase transition temperature in KNN can be effectively lowered by addition of CaTiO$_3$. The authors show that the orthorhombic to tetragonal transition temperature can be reduced by 1 wt% CaTiO$_3$ addition to below room temperature. This results in improved thermal stability and reduced temperature dependence of the piezoelectric response in the range $-50$ to 200°C, while maintaining acceptable piezoelectric properties $d_{33} = 210$ pC N$^{-1}$ [104, 105].
5. Bismuth perovskites

The low depolarization temperatures associated with polymorphic phase transformations in both the titanate and alkaline niobate perovskites remain the main obstacle in the commercialization of lead-free piezoelectric actuators. Increasing both the $T_d$ and $T_C$ should be achievable by creating solid solutions between the above materials and alternative high-$T_C$ end members such as the bismuth perovskites. The prototype bismuth perovskite is bismuth ferrite BiFeO$_3$, a rhombohedral ferroelectric with a large local spontaneous polarization ($P_s = 100 \, \mu \text{C cm}^{-2}$) and high Curie temperature ($T_C = 870 \, ^\circ\text{C}$) [106–109]. BiFeO$_3$ has been extensively studied owing to its multiferroic properties, simultaneously exhibiting antiferromagnetism and ferroelectricity. Recently, incorporation of bismuth perovskites into lead-based perovskites has been shown to be effective in increasing both $T_d$, exemplified by the BiScO$_3$–PbTiO$_3$ system [110, 111]. Reported piezoelectric coefficients and transition temperatures for the lead-free bismuth perovskites and their solid solutions are listed in Table 3.

5.1. Bismuth perovskite solid solutions with KNN

There have been several recent reports on the incorporation of bismuth perovskites into solid solutions with KNN. The solid solution BiScO$_3$–KNN has been synthesized with a large piezoelectric coefficient $d_{33} = 253 \, \text{pC cm}^{-1}$ and high Curie temperature $T_C = 351 \, ^\circ\text{C}$. Unfortunately, the orthorhombic–tetragonal transition temperature is largely unchanged giving $T_d$ of only 100 $^\circ\text{C}$ in this material. Bismuth ferrite solid solutions have also been investigated in KNN ceramics [112]. A complex KNN solid solution with BiFeO$_3$, SrTiO$_3$ and lithium has been reported with $d_{33} = 155 \, \text{pC cm}^{-1}$, $T_d = 30 \, ^\circ\text{C}$ and $T_C = 370 \, ^\circ\text{C}$ [113].

5.2. Bismuth ferrite–barium titanate solid solution

Previously, ceramic bismuth ferrite–barium titanate, BiFeO$_3$–BaTiO$_3$ solid solutions have been synthesized by several groups [114, 115]. The BiFeO$_3$–BaTiO$_3$ system has been shown to form a single phase perovskite solid solution within the complete compositional range, its room temperature symmetry is reported to be rombohedral at low BaTiO$_3$ content, switching to cubic (or perhaps pseudocubic) at 33 mol% BaTiO$_3$, and eventually becoming tetragonal for BaTiO$_3$ content greater than 92 mol%, as shown in figure 8. However, poor control of the bismuth volatility and iron oxidation state have generally led to low DC electrical resistivity and the inability to pole BiFeO$_3$–BaTiO$_3$ ceramics.

Recently, using MnO$_2$ modification and optimized solid state sintering conditions the current authors have shown that BiFeO$_3$–BaTiO$_3$ ceramics can be poled and show measurable piezoelectric coefficients in the range compositional range of 22–40 mol% BaTiO$_3$. These materials exhibit $d_{33}$ coefficients up to 115 pC N$^{-1}$, with a $T_C$ close to 600 $^\circ\text{C}$ and depolarization temperatures above 400 $^\circ\text{C}$ [116]. Additionally, high-field piezoelectric strain coefficients of up to $\sim 300 \, \text{pC cm}^{-1}$ are observed for the 33 mol% BaTiO$_3$ composition. However, large strain hysteresis suggests poor stability of poled domain state and significant domain switching contributions in the latter composition. Transmission electron microscopy (TEM) investigations in these materials reveal frustrated nanoscale domain patterns, shown in figure 9, which could explain the difficulty in obtaining stably poled ceramics.

Using a structural engineering approach the authors were able to induce large low field piezoelectric coefficients by application of large dc bias. Specifically, application of a 40 kV cm$^{-1}$ dc bias resulted in an enhanced piezoelectric response and a low-field $d_{33}$ coefficient of 150 pC N$^{-1}$ [117]. Following observations in other domain engineered ceramics, the application of a large dc bias in BiFeO$_3$–BaTiO$_3$ is believed to create an ‘engineered’ ordered domain state
leading to higher extrinsic and intrinsic contributions to
the piezoelectric coefficient in BF–BT ceramics. This is
in strong contrast to the expected suppression of extrinsic
contributions and reduction in the low field piezoelectric
coefficient typically observed in ferroelectric ceramics at large
dc bias. Evidence of this electric field induced engineered
domain state can been found in the weak residual banding of
the domain structure observed by TEM following high field
poling, as shown in figure 10.

6. Discussion and continued developments in
lead-free piezoceramics

The above review identifies many significant recent advances
in the search for lead-free materials for piezoceramic actuator
applications. However, it can be difficult to appreciate the
significant limitations associated with the vast majority of
these materials. Zhang et al have proposed the use of
graphs of $d_{33}$ over $T_d$ in order to make more reliable
comparisons both among and between lead-based and
lead-free piezoelectrics materials [4, 14, 118]. Such plots
provide a concise illustration of the relationship between
the room-temperature piezoelectric coefficient and phase
transition temperatures. They also provide an indication of the
temperature dependence and maximum usage temperatures
of the various piezoelectric materials and families of
materials.

Following this convention, the properties of the lead-free
materials summarized in this work are reported in figure 11.
Two separate graphs are provided the first including
only the lead-free materials and a second with a wide
range of lead-based materials superimposed. Reviewing
these graphs the following general trends are readily
identified. Firstly, within a given compositional family
the room-temperature $d_{33}$ coefficients increase as the $T_d$
decreases. (The inherent consequences reduced of reduced
$T_d$ are increased temperature dependence of $d_{33}$ and reduced
maximum usage temperature). Secondly, the majority of the
alkaline niobates (triangles) have depolarization temperatures
below 100 °C (associated with the orthorhombic–tetragonal
PPT) which is generally too low for these materials to
be of broad commercial interest (as is the case for pure
BaTiO$_3$). Thirdly, the titanates in general have both moderate
$d_{33}$ values (100–200 pCN$^{-1}$) and moderate depolarization
temperatures (100–300 °C). Fourthly, the bismuth perovskites
have among the highest depolarization temperatures reported
for any of the perovskite piezoceramic systems (including
lead-based materials). Finally, the lead-based materials
still maintain a clear performance advantage, universally
possessing the largest $d_{33}$ coefficients, while maintaining high
Curie temperatures, $T_C > 200$ °C.

In addition to the above general trends, these graphs
also suggest possible paths for future development. The
vertically stacked circles at $\sim 120^\circ C$ represent the effect of various structural engineering approaches in pure BaTiO$_3$ ceramics. While the $T_C$ of BaTiO$_3$ ceramics is still too low for these materials to be of broad interest, textured-domain engineered BaTiO$_3$ is the current benchmark piezoceramic material with a low field $d_{33} \sim 800$ pC/N. The stacked triangles at $\sim 25^\circ C$ also illustrated the effect of structural engineering, where a textured KNN material (LF4T) exhibits a significant enhancement of the $d_{33}$ coefficient over randomly oriented ceramics of the same composition (LF 4). Finally, the BiFeO$_3$–BaTiO$_3$ materials (stars) reveal enhancement of $d_{33}$ owing to field-induced ordering of the nanoscale domain structure in this system. On the basis of these strong enhancements observed in ‘structurally engineered’ piezoceramics it is suggested that more effort should be focused on understanding these effects and in applying them to existing materials rather than continued brute force compositional investigations.

**Figure 11.** Piezoelectric coefficient over depolarization temperature for (a) the various families of lead-free and (b) including lead-based piezoelectric ceramics.

### References

[1] Tressler J F, Alkoy S, Dogan A and Newnham R E 1999 *Composites A* 30 477
[2] Uchinoin K 1997 Present status of piezoelectric/electrostrictive actuators and remaining problems *Piezoelectric Actuators and Ultrasonic Motors* (Boston, MA: Kluwer)
[3] Setter N 2005 Ceramics( Laboratory) EPFL Swiss Federal Institute of Technology, Lausanne
[4] Randall C A, Kelnberger A, Yang G Y, Eitel R E and Shrodt T R 2005 *J. Electroceram.* 14 177
[5] Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric Ceramics* (New York: Academic)
[6] Sawaguchi E 1953 *J. Phys. Soc. Japan* 8 615
[7] Yamamoto T 1996 *Japan. J. Appl. Phys.* 1 35 5104
[8] Donnelly N J, Shrodt T R and Randall C A 2007 *J. Am. Ceram. Soc.* 90 490
[9] 2003 *Off. J. Eur. Union* 46 14
[10] 2003 *Off. J. Eur. Union* 46 4
[11] 2006 *California Health and Safety Code* 25214.9–25214.10.2
[12] 2000 *Off. J. Eur. Union* L 269 34
[13] Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, Nagaya T and Nakamura M 2004 *Nature* 432 84
[14] Zhang S J, Xia R and Shrodt T R 2007 *J. Electroceram.* 19 251
[15] Takenaka T, Nagata H and Hiruma Y 2008 *J. Appl. Phys.* 47 3787
[16] Shrodt T R and Zhang S J 2007 *J. Electroceram.* 19 111
[17] Tani T 1998 *J. Korean Phys. Soc.* 32 S1217
[18] Messing G L et al 2004 *Crit. Rev. Solid State. Mater. Sci.* 29 45
[19] Wada S, Yako K, Kakemoto H, Tsurumi T and Kiguchi T 2005 *J. Appl. Phys.* 98 014109
[20] Park S-E and Shrodt T R 1997 *J. Appl. Phys.* 82 1804
[21] Wada S, Takeda K, Muraishi T, Kakemoto H, Tsurumi T and Kimura T 2008 *Piezoelectrics* 373 11
[22] Park S E, Wada S, Cross L E and Shrodt T R 1999 *J. Appl. Phys.* 86 2746
[23] Gray R B 1949 **Transducer** and method of making the same *United States Patent Office* (USA: Erie Resistor Corporation)
[24] Roberts S 1947 *Phys. Rev.* 71 890
[25] Bechmann R 1956 J. **Electroceram.** Am. 28 347
[26] Takahashi H, Numamoto Y, Tani J, Matsuta K, Qiu J H and Tsurekawa S 2006 *Japan. J. Appl. Phys.* 2 45 L30
[27] Takahashi H, Numamoto Y, Tani J and Tsurekawa S 2006 *Japan. J. Appl. Phys.* 1 45 7405
[28] Takahashi H, Numamoto Y, Tani J and Tsurekawa S 2008 *Japan. J. Appl. Phys.* 47 8408
[29] Karaki T, Yan K and Adachi M 2007 *Japan. J. Appl. Phys.* 1 46 7035
[30] Karaki T, Yan K, Miyamoto T and Adachi M 2007 *Japan. J. Appl. Phys.* 46 197
[31] Popper P, Ruddenstien S N and Ingles T A 1957 **Trans. Br. Ceram. Soc.** 56 9
[32] Buhler C F 1962 J. **Chem. Phys.** 36 798
[33] Wada T, Toyoike K, Imanaka Y and Matsuo Y 2001 *Japan. J. Appl. Phys.* 1 40 5703
[34] Hiruma Y, Aoyagi R, Nagata H and Takenaka T 2005 *Japan. J. Appl. Phys.* 1 44 5040
[35] Hiruma Y, Marumo K, Aoyagi R, Nagata H and Takenaka T 2008 *J. Electroceram.* 21 296
[36] Hiruma Y, Nagata H and Takenaka T 2007 *Japan. J. Appl. Phys.* 1 46 1081
[37] Smolenskii G A, Isupov V A, Agranovskaya A I and Krainik N N 1961 Sov. Phys.—**Solid State** 2 2651
[38] Jones G O and Thomas P A 2002 *Acta Crystallogr.* B 58 168
[39] Roleder K, Suchanicz J and Kania A 1989 *Piezoelectrics* 89 1
[40] Suchanicz J 1995 *Piezoelectrics* 172 455

Sci. Technol. Adv. Mater. 11 (2010) 044302

Topical Review
[114] Itoh N, Shimura T, Sakamoto W and Yogo T 2007
Ferroelectrics 356 19
[115] Kumar M M, Srinivas A and Suryanarayana S V 2000
J. Appl. Phys. 87 855
[116] Leontsev S O and Eitel R E 2009 J. Am. Ceram. Soc. 92 2957
[117] Leontsev S O and Eitel R E submitted
[118] Shrou T R, Eitel R E and Randall C A 2002 Piezoelectric
Materials in Devices ed N Setter (Lausanne, Switzerland: EPFL, Swiss Federal Institute of Technology)
[119] Chang Y F, Poterala S F, Yang Z P, Trolier-McKinstry S and
Messing G L 2009 Appl. Phys. Lett. 95 232905
[120] Lei C and Ye Z G 2008 Appl. Phys. Lett. 93 042901
[121] Hollenstein E, Davis M, Damjanovic D and Setter N 2005
Appl. Phys. Lett. 87 182905
[122] Zhang J L, Zong X J, Wu L, Gao Y, Zheng P and Shao S F
2009 Appl. Phys. Lett. 95 022909
[123] Wang R, Xie R J, Hanada K, Matsusaki K, Kawanaka H,
Bando H, Sekiya T and Itoh M 2008 J. Electroceram. 21 263
[124] Guo Y P, Kakimoto K and Ohsato H 2004 Appl. Phys. Lett. 85 4121
[125] Hao J G, Chu R Q, Xu Z J, Zang G Z and Li G R 2009
J. Alloys Compd. 479 376
[126] Zuo R Z, Fu J and Lv D Y 2009 J. Am. Ceram. Soc. 92 283
[127] Safari A, Abazari M, Kerman K, Marandian-Hagh N and
Akdogan E K 2009 IEEE Trans. Ultrason. Ferroelectr.Freq.
Control 56 1586
[128] Fu J, Zuo R Z, Lv D Y, Liu Y and Wu Y 2010 J. Mater. Sci.,
Mater. Electron. 21 241
[129] Wang Y Y, Wu J G, Xiao D Q, Zhu J G, Yu P, Wu L and Li X
A 2008 J. Alloys Compd. 459 414
[130] Wang Y Y, Liu Q B, Wu J G, Xiao D Q and Zhu J G 2009
J. Am. Ceram. Soc. 92 755