**REVIEW ARTICLES**

**Na$_{1/2}$Bi$_{1/2}$TiO$_3$-based lead-free piezoceramics: a review of structure–property correlation**

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Piezoelectric materials transform electrical energy to mechanical energy and vice-versa making them technologically important as actuators, sensors and transducers in wide ranging applications. New regulations on prevention of hazardous materials in industrial applications have led to a great surge in research on environment friendly alternatives of the commercial Pb-based piezoelectrics – Pb(Zr, Ti)O$_3$. The field of lead-free piezoceramics has seen great advances in the last two decades. This review focuses on the current status of understanding of structure–property relationships in Na$_{1/2}$Bi$_{1/2}$TiO$_3$-based lead-free polycrystalline piezoceramics.

Keywords: Materials, piezoceramics, structure–property relationships.

The phenomenon of piezoelectricity, wherein a material develops voltage on application of mechanical force (direct piezoelectric effect) and changes dimension on application of electric field (converse piezoelectric effect), was discovered by Curie brothers in 1880 in single crystalline quartz minerals. Piezoelectric materials are currently being used in wide ranging applications such as transducers, actuators, pressor sensors, mechanical energy harvesting. The most common parameter to characterize a piezoelectric material is the piezoelectric coefficient $d$ defined as the ratio of strain and electric-field (for the converse phenomenon) or ratio of polarization and stress (for the direct phenomenon). The piezoelectric coefficient $d$ is commonly represented in units of pico-Coulomb/Newton (pC/N) for the direct-effect and picometre/Volt (pm/V) for the converse effect. Both units are thermodynamically (and dimensionally) equivalent.

The piezoelectric coefficient $d$ is a third rank tensor and has a maximum of 18 independent components. According to the Neuman’s principle, all the components are zero for a crystalline material, the structure of which has a centre of inversion symmetry. A fundamental requirement for a material to exhibit piezoelectricity is that its crystal structure should exhibit non-centrosymmetric point group. Among the 32 crystallographic point groups, 20 of them can show piezoelectric effect.

The piezoelectric coefficient of a single crystal quartz is 2 pC/N (ref. 4). Research on piezoelectric materials picked up after the discovery of ferroelectricity in BaTiO$_3$ during the Second World War. Ferroelectrics, first discovered in Rochelle salt in 1921 (ref. 5), are a sub-class of piezoceramics exhibiting spontaneous polarization, the direction of which can be reoriented by application of a strong electric field. Once subjected to a sufficiently strong electric field, the remanent polarization of a ferroelectric material makes it possible even for polycrystalline ferroelectric ceramic to behave as a piezoelectric material. Polycrystalline ceramics are easy to synthesize compared to single crystals and are attractive for mass scale production. A polycrystalline BaTiO$_3$ ceramic shows a longitudinal piezoelectric coefficient $d_{33}$ (polarization measured along the axis of the applied force) $\sim$190 pC/N (ref. 6) which is considerably larger than the piezoelectric coefficient of a single crystal quartz. However, after the discovery of better piezoelectric properties in pseudo-binary system PbTiO$_3$–PbZrO$_3$ (commonly abbreviated as PZT), interest in BaTiO$_3$-based ferroelectrics shifted towards the development of high dielectric constant materials.

Though ferroelectricity is known in many different families of inorganic and organic materials, the ABO$_3$ oxide ferroelectric perovskites have attracted most attention because of their significantly large piezoelectric properties. The highest symmetry phase of a perovskite structure is cubic (space group Pm-3m). Being centrosymmetric, this phase is paraelectric. On cooling below the Curie point (ferroelectric–paraelectric phase transition temperature), the paraelectric state transforms to a ferroelectric state along with a concomitant change in the crystal structure. For example, BaTiO$_3$ is paraelectric with a cubic structure above 130°C. Below 130°C, it transforms to a tetragonal (space group P4mm) ferroelectric phase. The spontaneous polarization in the tetragonal phase is along the [001] direction, i.e. parallel to the c-axis. On cooling further, BaTiO$_3$ undergoes two more structural transitions: orthorhombic ferroelectric phase (space group Amm2) with spontaneous polarization parallel to [110] direction and rhombohedral ferroelectric phase (space group R3m) with spontaneous polarization parallel to [111] direction. These directions are referred to with respect to the pseudocubic unit cell.

For over five decades, PZT-based piezoceramics have been the material of choice in most commercial applications. The piezoelectric properties of BaTiO$_3$ are superior to those of PZT, but the high dielectric constant of PZT has made it an attractive material for high capacitance applications. Recently, the development of lead-free piezoelectric materials has gained momentum due to the environmental concerns associated with the use of lead in electronic devices.

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applications. The importance of PZT is not only because of its large piezoelectric response but also because of good thermal stability of the piezoelectric properties. It derives this unique feature from the composition–temperature phase diagram which exhibits a nearly vertical morphotropic phase boundary (MPB) at ~52 mol% of PbZrO₃. The MPB of PZT separates rhombohedral and tetragonal phase fields⁶,⁷ and is therefore a composition driven inter-ferroelectric instability. This instability causes near flattening of the free-energy profile making it easy for the polarization to rotate on application of external electric-field and/or mechanical stress⁸ – the intrinsic piezoelectric response. The inter-ferroelectric instability also reduces the energy of the domain walls significantly, allowing their density and mobility to increase – the extrinsic contribution to piezoelectricity⁹,¹⁰. The discovery of considerable enhancement of the electromechanical response at the MPB in PZT has guided subsequent exploration of compositional engineering in other ferroelectric solid solutions.

**Lead-free piezoceramics**

In the past two decades increased environmental concerns and introduction of regulations aimed at restricting the use of toxic materials in industrial applications¹¹ have oriented the scientific community to focus on Pb-free piezoelectrics¹²–²¹. The first breakthrough that accelerated research on Pb-free piezoceramics, was the discovery of large piezoelectric effect (d³₃ ~ 450 pC/N) in textured ceramic of Li, Ta modified K₀.₅Na₀.₅NbO₃ (KNN)²². Over the period, higher d³₃ (~500 pC/N) has been reported even in non-textured KNN-based ferroelectric systems²³. Like the MPB in PZT, the compositional modification of KNN (by Li, Ta, Sb) is aimed at pushing the system towards an inter-ferroelectric instability at room temperature²⁴–²⁹. As with BaTiO₃, KNbO₃ (and KNN) exhibits the same sequence of structural transitions on cooling from high temperature: cubic (paraelectric) → tetragonal (ferroelectric) → orthorhombic → rhombohedral (ferroelectric). Analogous scenario in BaTiO₃ can be achieved by substitution of Zr, Sn and Hf at the Ti-site, leading to enhancement in the piezoelectric response from ~190 pC/N (unmodified BaTiO₃) to ~400 pC/N in the modified systems²⁵,²⁶. Interestingly, although the phase diagram is nearly the same, a notably larger d³₃ (~600 pC/N) was reported in Ca-modified Ba(Ti, Zr)O₃ (ref. 28), Ca-modified Ba(Ti, Sn)O₃ (refs 29–31) and Ca-modified Ba(Ti, Hf)O₃ (ref. 32) systems. Despite their large piezoelectric coefficient, BaTiO₃-based piezoceramics have the drawback of low Curie point (Tc ~ 80°C). This makes the system vulnerable to thermal depoling and deterioration in the piezoelectric response due to any unintentional increase in the temperature of the device during operation. In this context, though the KNN-based piezoelectrics are preferred because of their higher Curie point, their major drawback is the large dependence of the properties on the synthesis conditions. BiFeO₃ is another interesting lead-free ferroelectric compound with very high Curie point (~800°C)³³. Synthesis of pure BiFeO₃ is however difficult under normal conditions due to the presence of competing non-perovskite phases in the Bi₂O₃–Fe₂O₃ phase diagram³⁵. Another problem with BiFeO₃ is the large leakage current which makes poling difficult. These issues are resolved to a certain extent in solid solutions of BiFeO₃ with other perovskites³⁴–³⁶. Some solid solutions of BiFeO₃ show reasonably high d³₃ (~324 pC/N)³⁴ together with a high Curie point of 466°C, making them interesting for high temperature applications. One of the most extensively studied lead-free piezoelectric systems are based on the solid solutions of Na₀.₅Bi₀.₅TiO₃ (NBT) – sodium bismuth titanate. An important highlight of NBT-based piezoceramics is the large electrostrain (~0.7%) at ~60 kV/cm making them interesting for high performance actuator applications³⁷,³⁸. Because of the ease of synthesis, reproducibility of properties, and moderate depolarization temperature, NBT-based lead-free piezoceramics have been preferred in high-power ultrasonic devices³⁷. The complexity of the microstructure and crystal structure however, pose a great challenge for establishing structure–property relationships in NBT-based piezoceramics. Further in this review, a survey of the work with focus on structure-property correlations in NBT-based piezoceramics is presented.

**Na₀.₅Bi₀.₅TiO₃ (sodium bismuth titanate)**

Na₀.₅Bi₀.₅TiO₃ (NBT) was discovered in 1961 by Smolensky *et al.*³⁹ as a rhombohedral (space group R₃c) ferroelectric perovskite. NBT shows remnant polarization P_r = 38 μC/cm², coercive field in the range 50–60 kV/cm, d³₃ ~ 70 pC/N and Curie point 320°C (the temperature corresponding to permittivity maximum). The temperature dependence of dielectric constant of NBT exhibits two anomalies – a broad maximum at 320°C and a hump at ~200°C (refs 37–48). The hump at 200°C exhibits considerable frequency dispersion suggesting a relaxor ferroelectric behaviour⁴³,⁴⁴. Many reports exist on the anomalous changes in the physical properties of NBT in the temperature region 200–300°C (ref. 44). On heating, the remanent polarization decreases dramatically at 200°C, the depolarization temperature⁴⁵. The intermediate phase between 200°C and 320°C exhibits a pinched P–E hysteresis loop, a feature attributed to the onset of an anti-ferroelectric phase⁴⁶. However, neutron diffraction studies did not reveal any signature of anti-ferroelectric structure⁴⁷. In contrast to common ferroelectrics like BaTiO₃, PbTiO₃ or KNbO₃, the paraelectric phase exhibits a cubic (Pm-3m) structure, the paraelectric phase of NBT is a non-cubic tetragonal (space group P4bm)
structure comprising of in-phase tilt of the neighbouring octahedra along the c-axis of the tetragonal cell\(^{10}\). The cubic (Pm-3m) phase appears at higher temperature (~520°C)\(^{15}\). Cordero et al.\(^{52}\) reported sharp anomalies in the elastic compliance of NBT at ~550°C and 290°C and did not find any special structural origin of thermal depolarization at ~200°C. The two anomalies were attributed to the ferroelastic cubic (Pm-3m) – tetragonal (P4bm), ferroelectric P4bm–R3c transitions respectively. NBT exhibits a complex evolution of domain pattern in the temperature range 200–300°C, comprising of extensive twinning and formation of an intermediate orthorhombic (Pnma) structure on a shorter length scale\(^{53,54}\). The pinched P–E loop in this temperature region is attributed to this structural heterogeneity.

**Structural disorder in NBT at room temperature**

NBT exhibits a considerable degree of structural–polar disorder at room temperature. Balagurov et al.\(^{55}\) reported that the residual of the high temperature P4bm phase is found even at room temperature leading to an incommensurate modulation of the octahedral tilt. Evidence of long-period modulation in NBT was also reported by Thomas et al.\(^{56}\) using X-ray diffuse scattering study. Earlier, Kriel et al.\(^{57}\) reported the existence of local monoclinic displacement of the Na/Bi ion. Neutron pair distribution function study of NBT by Keeble et al.\(^{58}\) suggested a bifurcated polarization due to two distinctly different polar displacement of Bi\(^{75}\). First principles studies have revealed a complex interaction between local A-site cation ordering and octahedral tilt, and its influence on the relaxor ferroelectric behaviour of NBT\(^{59–61}\). The fundamental origin of the inherent structural disorder in NBT lies in the qualitatively different bonding characteristics of the Na–O (primarily ionic) and Bi–O (primarily covalent) bonds. Local structure studies by extended X-ray absorption fine structure (EXAFS) have revealed that the Bi–O bonds are 0.3 Å shorter than that revealed by structural analysis of X-ray/neutron diffraction data\(^{52,63}\). This confirms that the local environment of Bi is much distorted from that anticipated based on the average global structure. Aksel et al.\(^{64}\) have shown the structure when probed on the length scale of less than 10 Å to be different from the average structure as seen by diffraction techniques. A readjustment of the Bi–O bond distance was noted in poled specimen of NBT but not in the Ti–O distances, suggesting that strong electric field induces a correlated motion between the Bi-off centering and octahedral tilt\(^{65}\). \(^{23}\)Na and \(^{49}\)Ti nuclear magnetic resonance (NMR) spectroscopy studies have also revealed disorder on the A and B sites of NBT\(^{55,66}\), consistent with the other local structure studies.

The structural disorder on the local scale have a profound effect on the average structure perceived on the global scale. Gorfman and Thomas\(^{57}\) and Aksel et al.\(^{68}\) reported that the conventional rhombohedral (R3c) structural model was not enough to account for all the features of the high-resolution X-ray diffraction data of NBT. They proposed a monoclinic structure in the space group Cc. Levin and Reaney\(^{69}\) explained average monoclinic Cc structure in terms of assemblages of orthorhombic (average octahedral tilt \(\alpha\alpha\alpha\alpha\)) domains comprising of in-phase tilted octahedral region of few nano metres and comparatively longer antiphase tilted regions\(^{69}\). Rao et al.\(^{70}\) have shown signatures of Bragg peaks corresponding to R3c and Cc phases in high resolution synchrotron X-ray diffraction patterns of NBT (Figure 1). The relative fractions of the two phases are very sensitive to the treatment of the specimens by external electric-field and mechanical stress\(^{71,72}\). A correlation between the average Cc structure and high density of twinning was reported by Beanland and Thomas\(^{72}\). The regions in the specimen with less density of defect appear as rhombohedral\(^{72}\). Rao and Ranjan\(^{71}\) showed that poling of the NBT almost suppresses the monoclinic (Cc) phase and makes the global structure appear rhombohedral (R3c) (Figure 1). This is accompanied by suppression of the in-phase tilted local regions\(^{45}\) (Figure 1), and readjustment of the displacements of the Bi cation in conformity with the long-range rhombohedral structure\(^{62,73}\). Recently, it was shown that even the monoclinic Cc average structure of NBT changes to cubic when the grain size is reduced to ~2 microns\(^{74}\). Strong electric field could however bring about a cubic to rhombohedral distortion\(^{74}\). These studies confirm that the appearance of the different global structure cubic/moniclinic in the unpoled state of NBT is not associated with a structural transformation on the scale of unit cell but manifestations of different types of assemblages of the in-phase and anti-phase tilted regions\(^{69}\). In this context, Aksel et al.\(^{68}\) have shown that the local deviations from the average structure is more in the calcined NBT (smaller grain size) as compared to their sintered counterpart (larger grains).

**Off-stoichiometry studies**

Owing to the strong influence of structural disorder on the average structure and properties, it is anticipated that chemical modifications of NBT, including making it off-stoichiometric, would strongly influence its structure and properties\(^{75–85}\). Li et al.\(^{85}\) reported large oxygen ion conductivity in A-site off-stoichiometric NBT compositions. In general, Na-excess/Bi-deficient compositions decrease and Na-deficient/Bi-excess increase the resistivity\(^{75,78,84}\). Some reports show enhancement in piezoelectric response and lowering of the depolarization temperature in Bi-excess/Na-deficient compositions of NBT\(^{75,78,79,81}\). A detailed study on the effect of off-stoichiometry on the grain size, structure, electrical conductivity, impedance,
dielectric, ferroelectric and piezoelectric properties of NBT was recently reported by Mishra et al.\textsuperscript{75} (Figure 2 a, b). The $d_{33}$ increased from $\sim$80 pC/N for $x = 0$ to $\sim$100 pC/N for $x = -0.04$ in the off-stoichiometric composition series synthesized as per the chemical formula Na$_{0.5}$Bi$_{0.5+x}$TiO$_3$ (Figure 2 b). Mishra et al.\textsuperscript{75} reported a correlation between off-stoichiometry, grain size and $d_{33}$. Structural analysis of the poled specimens of the different off-stoichiometric compositions revealed a consistent increase in the degree of structural disorder with increasing Na-deficiency and Bi-excess specimens. The off-stoichiometric composition exhibiting the best piezoelectric response has an optimum fraction of the structural disorder coexisting with the field stabilized long-range ferroelectric order\textsuperscript{75}. A similar trend was reported with grain size of stoichiometric NBT\textsuperscript{74} and led the authors to argue that perhaps, in addition to the chemistry, comparatively reduced grain size in Na-deficient/Bi-excess off-stoichiometric NBT has a role to play in increasing the piezoelectric response\textsuperscript{74,75} (Figure 2 c).

**NBT-based solid solutions**

As stated above, the common compositional design approach in ferroelectric materials to enhance the piezoelectric
response is to induce an inter-ferroelectric instability at room temperature. Given that NBT is a rhombohedral (R3c) ferroelectric, it is anticipated that if it is modified by another ferroelectric perovskite compound with tetragonal structure, a composition driven rhombohedral-tetragonal inter-ferroelectric instability can be induced. Over the years, this strategy has been tried by researchers, an extensive compilation of which can be found in ref. 16. The two most prominent lead-free derivatives of NBT are the pseudo-binaries (1–\(x\))Na\(_{0.5}\)Bi\(_{0.5}\)TiO\(_3\)–(\(x\)BaTiO\(_3\) (NBT–BT)\(^{86–113}\) and (1–\(x\))Na\(_{0.5}\)Bi\(_{0.5}\)TiO\(_3\)–(\(x\)K\(_2\)O.\(_{0.5}\)Bi\(_{0.5}\)–TiO\(_3\) (NBT–KBT)\(^{114–135}\). Both BaTiO\(_3\) and K\(_2\)O.\(_{0.5}\)Bi\(_{0.5}\)–TiO\(_3\) are tetragonal (P4mm) ferroelectrics at room temperature and when increasingly dissolved in NBT are expected to show a rhombohedral–tetragonal instability. Takenaka et al.\(^{86}\) reported the first phase diagram of NBT–BT showing a morphotropic phase boundary at \(x = 0.06\) separating rhombohedral and tetragonal phase fields. The phase diagram of NBT–KBT with MPB at \(x = 0.2\) was first reported by Sasaki et al.\(^{115}\). The MPB compositions of NBT–BT and NBT–KBT show maximum dielectric and piezoelectric properties. The highest reported \(d_{33}\) for NBT–BT is 186 pC/N\(^{111}\) and for NBT–KBT is 207 pC/N\(^{125}\). It is important to point out that the maximum reported \(d_{33}\) in NBT-based piezoelectrics is significantly less when compared to the highest \(d_{33}\) reported in the BaTiO\(_3\)-based and KNN-based lead-free piezoelectric systems (\(d_{33} = 550–600\) pC/N). This issue has recently been dealt with by Adhikary and coworkers\(^{122–154}\), discussed in the next section. In contrast to the classical Pb-based MPB systems like PZT, the MPB composition of which shows a coexistence of tetragonal and rhombohedral/monoclinic phases on the global scale, the MPB compositions of NBT–BT and NBT–KBT exhibit a cubic-like structure\(^{87,91,94,98,132,133}\). The signature of the tetragonal and rhombohedral phases can however be seen in the Raman spectra\(^8\) and in the photoluminescence studies\(^{108,110}\) confirming that, as with the parent compound NBT\(^{59,72,75,84}\), the cubic like global structure of the MPB compositions of NBT–BT and NBT–KBT is associated with microstructural heterogeneity on a mesoscopic length scale. Similar to NBT, strong electric field induces a cubic to rhombohedral/rhombohedral + tetragonal structures\(^{91,98,104,109,133}\). Using the slope of the linear plots between permittivity and log–frequency as an indicator of polar-heterogeneity (Figure 3), Garg et al.\(^9\), Khatua et al.\(^{109}\) and Adhikary et al.\(^{133}\) argued that the structure–polar heterogeneity increases, which in turn increases the relaxor–ferroelectric characteristic, as the MPB is approached. These authors have also reported that the system tends to form a long-period modulation in the octahedral tilt configuration suggesting a sequential arrangement of the in-phase and anti-phase tilts\(^{98,133}\). Poling, however, dramatically suppresses the in-phase tilts and transforms the structure to rhombohedral or rhombohedral + tetragonal\(^{93,98,133}\) (Figure 3 d). The short ranged relaxor state to long-range ferroelectric transformation has also been reported by mechanical stress\(^{93,136}\). The signature corresponding to the long-period modulation persists in the tetragonal (P4mm) composition region (\(x > 0.07\)) until \(x = 0.20\). Rao et al.\(^{105}\) have demonstrated evidence of a new criticality at \(x = 0.2\) in the (1–\(x\))NBT–(\(x\))BT system where the coercivity and the spontaneous tetragonal strain exhibit a non-monotonic dependence with composition well within the tetragonal composition regime (Figure 4). Using neutron diffraction as a tool, Rao et al.\(^{105}\) showed that this new criticality is associated with the system’s transformation from a non-modulated tetragonal phase (for \(x > 0.2\)) to a modulated tetragonal phase (for \(x < 0.2\)). The occurrence of modulation in the octahedral tilt configuration depolarizes the system well before the diffuse dielectric anomaly temperature, i.e. inducing a relaxor–ferroelectric characteristic to the system.

As stated above, a unique feature of NBT-based piezoelectrics is that some compositional derivatives exhibit large high-field electrostrain compared to
Factors influencing thermal depoling in NBT-based piezoelectrics

The mechanism governing thermal depoling/depolarization of NBT and its chemical derivatives is a subject of considerable debate. The absence of any anomaly in the elastic compliance of NBT at ~200°C led Cordero et al.\textsuperscript{52} to suggest that the thermal depolarization is not driven by any kind of structural event. Aksel et al.\textsuperscript{144} on the other hand, related the thermal depolarization at 200°C to structural transition on a smaller length scale. Rao et al.\textsuperscript{45} have shown that the depoling process of NBT starts at ~150°C with the onset of in-phase octahedral tilt (Figure 5). For the two most investigated solid solutions, (1–x)Na\textsubscript{0.5}Bi\textsubscript{0.5}TiO\textsubscript{3}–xBaTiO\textsubscript{3} (NBT–BT) and others\textsuperscript{37,38,137–143}. A glimpse of this behaviour is observed even in the unmodified NBT when heated above the depolarization temperature (200°C). At 400°C, NBT shows a unipolar electrostrain of ~0.4% at 80 kV/cm (ref. 142). The role of different modifications is to bring down the ergodic–non-ergodic relaxor transition temperature to just below room temperature. Strong electric field at room temperature can induce a ferroelectric state causing large electrostrain. The reproducibility of the large electrostrain in different cycles is possible because the system is capable of reverting back to its ergodic relaxor–ferroelectric state when the field is reduced to zero. In the situation, this does not happen completely, the electrostrain reduces in successive cycles\textsuperscript{109}. The field induced ergodic–ferroelectric transitions are also interesting from the viewpoint of achieving enhanced electrocaloric response\textsuperscript{141}.\textsuperscript{110}.
$\text{(1-}y\text{)}\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-\text{yK}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT–KBT), exhibiting MPBs at $x = 0.06$ and $y = 0.20$ respectively, the depolarization temperature decreases sharply as the MPB is approached. This scenario contrasts with other MPB ferroelectric systems where no such remarkable change in the Curie point is reported at the MPB. Since the depolarization temperature is an indicator of the strength of the cooperative interaction of the neighbouring dipoles in a ferroelectric material, the anomalous dip in the depolarization temperature at the MPB of NBT–BT appears to indicate weakening of ferroelectricity at the MPB of NBT–BT. Recently Adhikary et al. have shown that as the MPB is approached, there is also an increasing intervention of a non-ferroelectric distortion in the form of in-phase tilt. The authors argue that the system’s propensity for this non-ferroelectric distortion causes weakening of ferroelectricity leading to a dramatic decrease in the depolarization temperature at the MPB. The authors also suggested that this could be one of the reasons which limits the weak-signal electromechanical properties of NBT-based systems.

With increasing technological interest in NBT-based piezoelectrics in high power applications, attempts are also being made to improve their depolarization temperatures. Zhang et al. reported a composite approach to enhance the depolarization temperature without significantly compromising the piezoelectric properties. The authors demonstrated that dispersed ZnO grains amid the ferroelectric grains of the MPB composition $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.06\text{BaTiO}_3$ (NBT–6BT) led to increase in the depolarization temperature by ~40°C (i.e. from 90°C to 130°C). They hypothesized that the free charge carriers in the semiconducting ZnO grains screen the depolarizing field in the ferroelectric grains and sustain ferroelectricity up to a relatively higher temperature. Mahajan et al. have questioned this electrostatic argument and argued in favour of a structural mechanism to explain thermal depolarization. Riemer et al. argued that the sustenance of ferroelectricity up to higher temperature in the 0–3 NBT–6BT/ZnO composite is caused by deviatoric stress field due to difference in the thermal expansion coefficients of ZnO and the ferroelectric grains. A noticeable increase in the depolarization temperature has also been reported in non-composite specimens such as in Zn-doped NBT–6BT thereby suggesting that the composite nature of the specimen need not be the primary factor influencing the delay in thermal depolarization of ZnO modified NBT-based piezoceramics. Recently Khatua et al. demonstrated that the depolarization temperature of NBT-based piezoceramics is grain-size dependent. They established a coupled microstructural (grain size)–structural mechanism and show that the large grain-sized NBT specimens show higher depolarization temperature as compared to NBT with small grain size. Khatua et al. demonstrated that the increase in the depolarization temperature in large grain size specimen is caused by larger grains able to stabilize large ferroelectric distortion after poling. The authors rationalized that instead of the screening-field stabilizing the ferroelectric phase in ZnO-doped NBT, it is the larger grain size of...
Figure 6.  

**a–c**, Depolarization temperature/Curie point as a function of composition around the respective morphotropic phase boundaries of (a) \((1-x)\text{Na}_0.5\text{Bi}_0.5\text{TiO}_3-(x)\text{BaTiO}_3\), (b) \(\text{Pb(Zr}_{x}\text{Ti}_{1-x})_\text{O}_3\) and (c) \((1-x)\text{BaZr}_{0.8}\text{Ti}_{0.8}\text{O}_3-(x)\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3\) piezoelectric systems. Note the anomalous dip at the MPB in the NBT–BT and not so in the other two systems. 

**d**, The composition dependence of evolution of the 0.5\{310\} and 0.5\{311\} superlattice peaks as observed in the neutron powder diffraction of the specimens. 

**e**, The peak intensity of these two superlattice peaks plotted on a normalized scale (treating the background corrected peak count of the strongest reflection as 100). Note the significant increase in the intensity of the 0.5\{310\} superlattice peak corresponding to in-phase octahedral tilt at the MPB \((x = 0.06)\). A concomitant decrease in the intensity of the 0.5\{311\} superlattice peak, corresponding to the \(R3c\) phase is also evident at the MPB composition. 

Figure 7.  

Scanning electron microscope images (secondary electron image) of NBT sintered at (a) 1150°C and (b) 1200°C. (c) Thermal depoling of the two specimens by measuring \(d_{33}\) as a function of the thermal aging temperature. Note the higher depolarization temperature of the NBT1200 with significantly larger grain size. 

Summary and outlook

Regulations on the restricted use of hazardous materials in several countries across the world have given a great
thrust to research and development in Pb-free piezoelectrics. While some lead-free compositions have found applications in niche products, a PZT like universal lead-free piezoelectric material system for wide ranging applications is still not on the horizon. This urgency has however helped in discovering new Pb-free systems with large electromechanical properties, and helped in developing deeper scientific understanding of some of the complex issues related to structure–property correlations. Regarding NBT-based piezoceramics, it is now evident complex issues related to structure–property correlations. As highlighted in this review, an important structural feature associated with structural–polar disorder is the system’s propensity for stabilizing in-phase octahedral tilt which is incompatible with ferroelectric order. Recent research shows that this propensity is maximum at the MPB of NBT–BT and this tilt disorder which can suppress the system propensity for this in-phase octahedral tilt. At the same time, this tilt disorder appears to be playing an important role in enabling the system to exhibit large high-field electrostrain making them interesting for high performance actuator applications.

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