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)O3. 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 Na1/2Bi1/2TiO3-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 minerals1. Piezoelectric materials are currently being used in wide ranging applications such as transducers, actuators, pressor sensors, mechanical energy harvesting2. 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) equivalent1. 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 effect2.

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 BaTiO3 during the Second World War5. Ferroelectrics, first discovered in Rochelle salt in 1921 (ref. 5), are a sub-class of piezoelectrics 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 production6. A polycrystalline BaTiO3 ceramic shows a longitudinal piezoelectric coefficient d33 (polarization measured along the axis of the applied force) ~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 PbTiO3–PbZrO3 (commonly abbreviated as PZT)8, interest in BaTiO3-based ferroelectrics shifted towards the development of high dielectric constant materials7. Though ferroelectricity is known in many different families of inorganic and organic materials, the ABO3 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, BaTiO3 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, BaTiO3 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] direction6. 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 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 applications1 have oriented the scientific community to focus on Pb-free piezoceramics12–21. The first breakthrough that accelerated research on Pb-free piezoceramics, was the discovery of large piezoelectric effect ($d_{33} \sim 450 \text{ pC/N}$) in textured ceramic of Li, Ta modified K0.5Na0.5NbO3 (KNN)22. Over the period, higher $d_{33}$ (~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 temperature24–26. As with BaTiO3, KNbO3 (and KNN) exhibits the same sequence of structural transitions on cooling from high temperature: cubic (paraelectric) $\rightarrow$ tetragonal (ferroelectric) $\rightarrow$ orthorhombic $\rightarrow$ 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 $d_{33}$ (~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 ($T_C \sim 80^\circ\text{C}$). 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 piezoceramics 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)23. Synthesis of pure BiFeO3 is however difficult under normal conditions due to the presence of competing non-perovskite phases in the Bi2O3–Fe2O3 phase diagram33. 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 $d_{33}$ (~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 piezoelectrics 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 $P_r = 38 \mu\text{C/cm}^2$, coercive field in the range 50–60 kV/cm, $d_{33} \sim 70 \text{ pC/N}$ 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 temperature44. 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 phase45. However, neutron diffraction studies did not reveal any signature of anti-ferroelectric structure46. 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\textsuperscript{30}. The cubic (Pm-3m) phase appears at higher temperature (~520°C)\textsuperscript{35}. Cordero et al.\textsuperscript{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\textsuperscript{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.\textsuperscript{55} reported that the residue 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.\textsuperscript{56} using X-ray diffuse scattering study. Earlier, Kriel- sel et al.\textsuperscript{57} reported the existence of local monoclinic displacement of the Na/Bi ion. Neutron pair distribution function study of NBT by Keeble et al.\textsuperscript{58} suggested a bifurcated polarization due to two distinctly different polar displacement of Bi\textsuperscript{73}. 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\textsuperscript{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\textsuperscript{62,63}. This confirms that the local environment of Bi is much distorted from that anticipated based on the average global structure. Aksel et al.\textsuperscript{65} 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\textsuperscript{66}. 23Na and 49Ti nuclear magnetic resonance (NMR) spectroscopy studies have also revealed disorder on the A and B sites of NBT\textsuperscript{65,66}, 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\textsuperscript{77} and Aksel et al.\textsuperscript{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\textsuperscript{78} explained average monoclinic Cc structure in terms of assemblages of orthorhombic (average octahedral tilt a’a c’') domains comprising of in-phase tilted octahedral region of few nano metres and comparatively longer antiphase tilted regions\textsuperscript{69}. Rao et al.\textsuperscript{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\textsuperscript{71,72}. A correlation between the average Cc structure and high density of twinning was reported by Beanland and Thomas\textsuperscript{72}. The regions in the specimen with less density of defect appear as rhombohedral\textsuperscript{72}. Rao and Ranjan\textsuperscript{71} showed that poled 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\textsuperscript{45} (Figure 1), and readjustment of the displacements of the Bi cation in conformity with the long-range rhombohedral structure\textsuperscript{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\textsuperscript{74}. Strong electric field could however bring about a cubic to rhombohedral distortion\textsuperscript{74}. These studies confirm that the appearance of the different global structure cubic monoclinic 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\textsuperscript{69}. In this context, Aksel et al.\textsuperscript{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\textsuperscript{75–85}. Li et al.\textsuperscript{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\textsuperscript{77,78,84}. Some reports show enhancement in piezoelectric response and lowering of the depolarization temperature in Bi-excess/Na-deficient compositions of NBT\textsuperscript{75,78,79,81}. A detailed study on the effect of off-stoichiometry on the grain size, structure, electrical conductivity, impedance,
Figure 1. a. Selected profiles of the whole pattern Rietveld fitted high-resolution synchrotron X-ray (wavelength = 0.39991 Å) powder diffraction pattern of unpoled and poled Na$_{0.5}$Bi$_{0.5}$TiO$_3$ specimens. The diffraction pattern on the poled specimen was recorded after breaking the poled pellet to powder to avoid preferred orientation effect. For the unpoled specimen the ground powder obtained from pellet was annealed at high temperature to get rid of stress induced structural changes. The arrows in the first row show unaccounted Bragg peaks corresponding to the rhombohedral phase when the data was fitted with monoclinic (Cc) phase. The patterns in the second row shows pattern of poled NBT fitted with single phase $R_{3c}$ structural model. All features in the diffraction pattern of the unpoled specimen are nicely accounted for with the Cc + $R_{3c}$ phase coexistence model as shown in the third row. b. The HRTEM and electron diffraction patterns of unpoled and poled NBT corresponding to [111] (shown at top corners of the corresponding HRTEM image) and [130] (shown at the bottom corners of the corresponding HRTEM image) zone axes. Important to note that the HRTEM of the unpoled NBT is hazy and that of the poled specimen show relatively well defined lattice fringes. The [111] zone axis diffraction pattern of unpoled NBT shows ½{odd odd even} type superlattice spots which are absent in the pattern of poled specimen. Also, diffuse streaks between Bragg spots are evident in the [130] zone axis pattern of unpoled specimen and not in the poled specimen.75

Dielectric, ferroelectric and piezoelectric properties of NBT was recently reported by Mishra et al.75 (Figure 2 a, b). The $d_{33}$ increased from ~80 pC/N for $x = 0$ to ~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.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.75 A similar trend was reported with grain size of stoichiometric NBT74 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 response74,75 (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)Na0.5Bi0.5TiO3−(x)BaTiO3 (NBT–xBT)86–113 and (1−x)Na0.5Bi0.5TiO3−(x)K0.5Bi0.5−TiO3 (NBT–xKBT)114–135. Both BaTiO3 and K0.5Bi0.5−TiO3 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–xBT showing a morphotrophic phase boundary at x = 0.06 separating rhombohedral and tetragonal phase fields. The phase diagram of NBT–xKBT with MPB at x ~ 0.20 was first reported by Sasaki et al.115. The MPB compositions of NBT–xBT and NBT–xKBT show maximum dielectric and piezoelectric properties. The highest reported d33 for NBT–BT is 186 pC/N111 and for NBT–KBT is 207 pC/N125. It is important to point out that the maximum reported d33 in NBT-based piezoelectrics is significantly less when compared to the highest d33 reported in the BaTiO3-based and KNN-based lead-free piezoelectric systems (d33 ~ 550–600 pC/N). This issue has recently been dealt with by Adhikary and co-workers132–154, 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 structure87,91,94,98,132,133. The signature of the tetragonal and rhombohedral phases can however be seen in the Raman spectra87,91,94,98,132,133 confirming that, as with the parent compound NBT59,72,75,84, 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 structures91,98,104,109,133. Using the slope of the linear plots between permittivity and log–frequency as an indicator of polar-heterogeneity (Figure 3), Garg et al.95, 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 tilts98,133. Poling, however, dramatically suppresses the in-phase tilts and transforms the structure to rhombohedral or rhombohedral + tetragonal93,98,133 (Figure 3 d). The short ranged relaxor state to long-range ferroelectric transformation has also been reported by mechanical stress93,136. 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...
Figure 3.  

- **a**, Temperature dependence of relative permittivity of (1–x)Na0.5Bi0.5TiO3–(x)BaTiO3 for different BaTiO3 concentration (x values shown in the plot).
- **b**, The permittivity as a function of log-frequency for a representative composition x = 0.065 (in the MPB region) measured at room temperature. The slope of the such plots as a function of BaTiO3 concentration (x) is shown in (c). Important to note that this slope is maximum for the MPB compositions suggesting a greater degree of polar-heterogeneity at the MPB.
- **d**, Rietveld fitted neutron powder diffraction patterns of two close by MPB compositions x = 0.06 and x = 0.0675 using R3c + P4bm phase coexistence model. The misfit regions are highlighted in the insets and with arrow in the plot. The additional superlattice peak marked with arrow suggest the need for considering higher order modulation in the octahedral tilt configuration93.

Figure 4.

- **Composition dependence of (a) tetragonality and (b) coercive-field of (1–x)BaTiO3–(x)Na0.5Bi0.5TiO3. A maximum in both the quantities can be seen at x = 0.80.**
- **b** The composition evolution of the neutron powder diffraction pattern of (1–x)BaTiO3–(x)Na0.5Bi0.5TiO3. The $\frac{1}{2}[310]$ superlattice peak corresponding to in-phase octahedral tilt appears for x > 0.80. The reduction in the tetragonality and coercive field for x > 0.80 is therefore attributed to the onset of the in-phase tilt104.

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.52 to suggest that the thermal depolarization is not driven by any kind of structural event. Aksel et al.144 on the other hand, related the thermal depolarization at 200°C to structural transition on a smaller length scale. Rao et al.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)Na0.5Bi0.5TiO3–xBaTiO3 (NBT–BT) and others37,38,137–143. 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 cycles109. The field induced ergodic–ferroelectric transitions are also interesting from the viewpoint of achieving enhanced electrocaloric response141.
(1−\(y\))Na_{0.5}Bi_{0.5}TiO_{3−y}K_{0.5}Bi_{0.5}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\(^{132,133,134}\). This scenario contrasts with other MPB ferroelectric systems where no such remarkable change in the Curie point is reported at the MPB\(^{132,134}\). 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\(^{132–134}\) 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 (Figure 6 \(d\) and \(e\)). 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\(^{17}\), attempts are also being made to improve their depolarization temperatures\(^{145–150}\). Zhang et al\(^{148}\) 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 0.94Na_{0.5}Bi_{0.5}TiO_3–0.06BaTiO_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.\(^{146}\) have questioned this electrostatic argument and argued in favour of a structural mechanism to explain thermal depolarization. Riemer et al.\(^{149}\) 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 notable increase in the depolarization temperature has also been reported in non-composite specimens such as in Zn-doped NBT–6BT\(^{150}\) 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.\(^{107}\) demonstrated that the depolarization temperature of NBT-based piezoceramics is grain-size dependent (Figure 7). 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.\(^{107}\) 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\(^{107}\), 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) \(\text{Pb}(\text{Zr}_{x}\text{Ti}_{1-x})\text{O}_3\) 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.\(^{15}\).

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.\(^{16}\).

the ZnO-modified specimens and the corresponding stabilization of the relatively large ferroelectric distortion after poling in such specimens which causes the increase in the depolarization temperature.

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 piezoceramics. 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 that a highly complex inter-relationship exists between synthesis conditions, grain size, length scale dependent crystal structures and physical properties. 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 NBT–KBT systems. The consequent weakening of the strength of ferroelectric interaction causes lowering of the depolarization temperature and, perhaps, also not allowing the system to develop large piezoelectric response (comparable to what has been achieved in other Pb-free piezoceramics). It is anticipated that large piezoelectric response in NBT-based piezoceramics requires strategies 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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ACKNOWLEDGEMENTS. R.R. thanks the Science and Engineering Research Board (SERB) of the Department of Science and Technology, Govt of India for financial support (Grant No. EMR/2016/001457); Council of Scientific and Industrial Research, and the IISc for supporting research on piezoceramics.

Received 2 January 2020; accepted 24 January 2020

doi: 10.18520/cs/v118/i10/1507-1519