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BiFeO$_3$-BaTiO$_3$: A new generation of lead-free electroceramics

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Lead-based electroceramics such as Pb(Zr,Ti)O$_3$ (PZT) and its derivatives have excellent piezoelectric, pyroelectric and energy storage properties and can be used in a wide range of applications. Potential lead-free replacements for PZT such as potassium sodium niobate (KNN) and sodium bismuth titanate (NBT) have a much more limited range of useful properties and have been optimized primarily for piezoelectric applications. Here, we review the initial results on a new generation of lead-free electroceramics based on BiFeO$_3$-BaTiO$_3$ (BF-BT) highlighting the essential crystal chemistry that permits a wide range of functional properties. We demonstrate that with the appropriate dopants and heat treatment, BF-BT can be used to fabricate commercially viable ceramics for applications, ranging from sensors, multilayer actuators, capacitors and high-density energy storage devices. We also assess the potential of BF-BT-based ceramics for electrocaloric and pyroelectric applications.

Keywords: BiFeO$_3$-BaTiO$_3$; lead-free; piezoelectrics; energy storage; dielectrics; capacitors.

1. Introduction

Electroceramics is a class of materials used for their unique electrical, optical and magnetic properties in communications, energy conversion and storage, electronics and automation. Electroceramics have subclasses which include dielectrics, piezoelectrics, pyroelectrics, ferroelectrics, ion conductors, and magnetic ceramics. Currently, the market for electroceramics is dominated by BaTiO$_3$ (BT) and Pb(Zr,Ti)O$_3$ (PZT). BaTiO$_3$ is utilized in dielectric applications in multilayer ceramic capacitors (MLCCs), produced in trillions of parts per year, whereas PZT is the basis for pyro-, piezo- and ferroelectric application as well as novel energy storage technology at the antiferroelectric/ferroelectric (AFE/FE) phase boundary within the PZT phase diagram.

2. Piezoelectricity and Lead Zirconate Titanate

Piezoelectricity was first discovered in quartz by Pierre and Jacques Curie in 1880 who determined that mechanical stress generated electric charge on the surface of quartz, now referred to as the direct piezoelectric effect. The inverse piezoelectric effect was mathematically deduced from fundamental thermodynamic principles by Gabriel Lippmann in 1881 and experimentally confirmed by the Curie brothers. Over the next few decades, 20 natural crystals were found to show piezoelectricity and their properties were rigorously defined using tensor analysis. The first application using piezoelectric material was conducted by Paul Lengvin in 1917 during World War I when quartz was used in ultrasonic submarine detectors, called sonar. During World War II, BaTiO$_3$ was simultaneously discovered in USA, Russia, and
Japan. Since BaTiO\textsubscript{3} has much higher dielectric and piezoelectric properties than natural materials, the development of piezoelectric materials was accelerated, leading to the discovery of PZT after World War II.\textsuperscript{4,5} PZT has a morphotropic phase boundary (MPB), separating rhombohedral (R) and tetragonal (T) phase, and hence shows high piezoelectric properties with high Curie temperature (T\textsubscript{C}, Fig. 1). Since this compositionally driven phase transition is nearly independent of temperature, PZT has been widely applied to many applications. T and R phases have six spontaneous polarization directions along $\langle 001 \rangle$ and eight along $\langle 111 \rangle$, respectively. Therefore, at the MPB, there exist many possible polarization directions and hence high piezoelectric properties are generated. In addition, Noheda \textit{et al.}\textsuperscript{6,9} reported a monoclinic (M) phase between the T and R phase in PZT in 1999. The M phase has 24 possible polarization directions which enhance the electromechanical properties. The properties of commercial PZTs are controlled by dopants which are broadly categorized as soft PZT (donor doped) and hard PZT (acceptor doped).\textsuperscript{10-14} These features have made PZTs the most widely used piezoelectrics to date.

3. Lead-Free Piezoelectrics

Following increased environmental awareness during the latter part of the 20th century, lead has become subject to increasing legal restraints that prohibit its usage, alongside volatile and endangered raw materials and hence they are considered environmentally friendly, sustainable and easy to process.

![Fig. 1. (a) Phase diagram and (b) electromechanical properties of Pb(Zr,Ti)O\textsubscript{3} (PZT).](image-url)
Fig. 2. (a) Comparison of $d_{33}$ at 25°C among developed ($K_{0.44}N_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ (LF) ceramics, and conventional PZT and lead free ceramics as a function of $T_C$. (b) Temperature dependences of $d_{33}$ for the textured (LF4T), nontextured (LF4) and PZT4 ceramics. Inset, electric-field-induced strain curve for LF4T, LF4 and PZT4 ceramics at 25°C.10

Fig. 3. Field-induced strain in $(0.94-x)Bi_{0.5}Na_{0.5}TiO_3-xBi_dTiO_3-xK_{0.5}Ni_{0.5}NbO_3$ (BNT-BT-KNN) ceramics. (a) Bipolar strain curves of BNT-BT-xKNN with $x = 0$, 0.02, and 0.04. (b) Unipolar strain curves of BNT-BT-KNN with $x = 0$, 0.02, and 0.04 in comparison to that of commercial soft PZT.32

Fig. 4. (a) Comparison of $d_{33}$ among 0.50Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$-0.50(Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ (BZT-50BCT) and other lead-free piezoelectrics and PZT family. (b) Electric-field-induced strain of BZT-50BCT in comparison with several typical PZT ceramics.42

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4. The BiFeO$_3$-BaTiO$_3$ System

The ceramics discussed in Sec. 3 show great promise for the development of lead-free piezoelectrics, but PZT also exhibits several further useful physical properties and can be used in different applications. Ideally, therefore an alternative lead-free system is required which can be used not only as a piezoelectric but also in other applications, potentially simplifying industrial production of lead-free electroceramics. BiFeO$_3$-BaTiO$_3$ (BF-BT) ceramics have recently emerged as a contender to replace PZT. BaTiO$_3$ and BiFeO$_3$ have $T$ and $R$ structures, respectively, at RT with the latter having a particularly high $T_C$ (825°C).48–50 As early as 1964, Venetsev et al.51 claimed that BF-BT formed a continuous solid solution at RT with three crystal structures: $R$ (100-67% BF), $C$ (67-7.5% BF) and $T$ (7.5-0% BF), which was later confirmed by Kumar et al.52 In 2009, Leontsev and Eitel53 gave a revised phase diagram for BF-BT system, Fig. 5, based on temperature dependence of dielectric constant ($\varepsilon_r$) and differential scanning calorimetry (DSC) measurements. They reported a broad, temperature-independent MPB (0.25-0.4BT) between $R$ and $C$ phases, with enhanced piezoelectricity. Subsequently, Lee et al.54 reported a PZT-like $R$-$T$ MPB in quenched BF-BT based ceramics, with high $d_{33} = 402 \text{pC/N}$ and $T_C = 454°C$, as shown in Fig. 6.

There is clear similarity between PZT and BF-BT solid solutions with a general trend from $R$ to $T$ as BT and PT concentration increase, respectively. However, in BF-BT, both the A- and B-sites are occupied by more than one ionic species as opposed to just the B-site in PZT. This rather obvious statement accounts for the differences in the compositional phase transformations between PZT and BF-BT. In PZT, Ti and Zr compete to influence the displacement of the contiguous Pb-site with its highly polarizable lone pair of electrons. In contrast in BF-BT, Ba acts as a large blocking ion for displacements of the Bi lone pair species. On the B-site, Fe compete with Ti displacements. The presence of competition for uniform displacements on each site results in a greater driving force for the formation of short-range ordered pseudosymmetric structures, as observed by Leontsev and Eitel53 and subsequent researchers. There is therefore, a greater tendency in the system for the formation of broad relaxor-like dielectric behavior than within PZT. Although this may not be ideal to obtain large $d_{33}$, it does not preclude a high strain electrostrictive response (large $d_{33}/C_{33}$) and is ideal for high energy density storage, electrocaloric and possibly pyroelectric applications.

The many recent publications over the last decade, as shown in Fig. 7, indicate that the BF-BT system is one of most promising candidates for lead-free ceramics. In this

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Fig. 5. Phase diagram of BiFeO$_3$-BaTiO$_3$ (BF-BT) solid solution.53

Fig. 6. (a) Suggested phase diagram of BiFeO$_3$-BaTiO$_3$ (BF-BT) system; (b) rhombohedral distortions (90°-$\alpha_R$) and phase volume fractions of furnace-cooled 0.67BiFeO$_3$-0.33BaTiO$_3$ (BF33BT), water-quenched BF33BT, 3%Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ (BZT) doped BF33BT (BF33BT-3BZT) and 3%BiGaO$_3$ (BG) doped BF33BT (BF33BT-3BG) ceramics.54
paper, we will review the current development of BF-BT lead-free ceramics, focusing on the crystal/domain structure, compositional inhomogeneity, piezoelectricity and energy storage properties. We demonstrate that with the appropriate dopants and heat treatment, BF-BT can be used to fabricate commercially viable ceramics for applications ranging from sensors, multilayer actuators, high temperature capacitors and high-density energy storage capacitors with potential for, but as yet unexplored, electrocaloric and pyroelectric applications.

5. BiFeO$_3$-BaTiO$_3$ Based Ceramics

5.1. Crystal/domain structure and compositional inhomogeneity

5.1.1. Crystal structure

Furnace cooled BF-BT solid solutions are widely considered to have an $R$-$C$ phase boundary (albeit broad) at which the electromechanical properties are optimized.$^{51-54}$ Gotardo et al.$^{55}$ are one of the few authors who disagree with this perception and have ascribed $x$BF-(1-$x$)BT ($0.3 \leq x \leq 0.9$) ceramics to a combination of $R3c$ and $Cm$ phases, as shown in Fig. 8. Moreover, Lee et al.$^{54}$ reported an MPB in quenched Ga-doped BF-BT between $R3c$ and $P4mm$ (Fig. 6), with $d_{33} = 402$ pC/N. Despite these observations, the general consensus is that doping BF-BT pushes the system towards relaxor behavior accompanied by promotion of a core-shell microstructure,$^{56}$ particularly if samples are furnace cooled.

Even though the low signal $d_{33}$ reported by Lee et al.$^{54}$ has not to date been repeated, many authors have observed large $S_{\text{max}}$ and (high signal) $d_{33}$ in quenched compositions with BiMeO$_3$ dopants, such as Bi(Zn$_{2/3}$Nb$_{1/3}$)$_3$O$_3$ (BZN), Bi(Mg$_{2/3}$Nb$_{1/3}$)$_3$O$_3$ (BMN) and BiScO$_3$ (BSc).$^{56-58}$ Only Murakami et al.$^{56,57}$ deliberately eradicated quenching using BMN and BSc as dopants to give high $S_{\text{max}} (> 0.4\%)$ in furnace cooled ceramics in which $R$ and $C$ phases ($C$ dominant) coexisted. These authors argued that avoiding quenching was advantageous for industrial manufacturing. Overall, these reports point to the potential of the BF-BT ceramics as high strain actuators but demonstrate that the structure and thus properties are sensitive to dopant concentration, type and heat treatment.

5.1.2. Domain structure

Ferroelectric domain structure and its evolution as a function of composition, temperature and electric field are critical to
understanding the performance of any given ferroelectric solid solution. Mori et al.\textsuperscript{59,60} examined the domain structure evolution of BF-BT across the $R$ to $C$ transformation and found that the lamellar domain morphology changed from well-defined herringbone type in $0.8\text{BF}-0.2\text{BT}$ to a more complex configuration in $0.72\text{BF}-0.28\text{BT}$, to tweed-like small domains in $0.67\text{BF}-0.33\text{BT}$, and then to a nano-domain structure for $0.4$ and $0.5\text{BT}$, as shown in Fig. 9. Even though $d_{33}$ is a maximum at the $R$ to $C$ phase boundary, the highest $S_{\text{max}}$ and $d_{33}$ appear in compositions with a dominant nano-domain structure. Wang and Murakami et al.\textsuperscript{56,61} have elucidated such correlations through systematic TEM observations in Nd- and BMN-doped BF-BT compositions (Figs. 10 and 11) but further work is required to understand the field induced transition behavior in these complex systems. Kim et al.\textsuperscript{62} compared the domain structure between furnace-cooled and air-quenched $0.75\text{BF}-0.25\text{BT}$ and showed that the air-quenched sample contained more regular domain structure than furnace cooled, as shown in Fig. 12. This data is consistent with a larger piezoelectric response and implies that in quenched samples composition/microstructure/defect structure may be very different from furnace cooled. Most authors note that quenching tends to suppress the core-shell structure, hinting at complex changes to phase equilibria as a function of temperature.

5.1.3. Compositional inhomogeneity

Compositional inhomogeneity is often observed in doped BF-BT ceramics as evidenced by a core-shell microstructure composed of dark and light contrast relating to Ba/Ti-rich and Bi/Fe-rich regions in backscattered electron images (BSE, Figs. 13(a)–13(c)) as confirmed by elemental mapping (Figs. 13(d)–13(k)), transmission electron microscopy (TEM), temperature dependence of $\varepsilon_r$ and impedance spectroscopy.\textsuperscript{56–58,63–67} Wang et al.\textsuperscript{58} recently examined the core-shell microstructure of BZN-doped BF-BT by TEM and found that the Bi/Fe-rich core regions had $\{1/21/21/2\}$ superstructure reflections consistent with an $R3c$ phase while Ba/Ti-rich shell regions were composed of a relaxor-like, nano-domain structured $C$ phase, commensurate with a diffuse frequency-dependent Curie maximum, Fig. 14. Murakami et al.\textsuperscript{56,57} observed compositional inhomogeneity in Bi(Me)\textsubscript{2}O\textsubscript{3}-doped BF-BT (Me=Y, Ga, Al, Sc\textsubscript{1/2}Y\textsubscript{1/2}, Mg\textsubscript{2/3}Nb\textsubscript{1/3}, Sc, Zn\textsubscript{2/3}Nb\textsubscript{1/3}, Zn\textsubscript{1/2}Ti\textsubscript{1/2}) and proved that

![Fig. 9. Domain evolution and diffraction patterns of (1 – x)BF-xBT.\textsuperscript{59,60}](image)

![Fig. 10. TEM images of the domain structure in 0.7BF-0.3BT, 5%Nd-doped 0.7BF-0.3BT and 10%Nd-doped 0.7BF-0.3BT.\textsuperscript{61}](image)
Fig. 11. TEM images and diffraction patterns in Bi(Mg$_{2/3}$Nb$_{1/3}$)O$_3$ (BMN) doped BF-BT (a) 0.63BF-0.32BT-0.05BMN and (b) 0.7BF-0.25BT-0.05BMN.$^{56}$

Fig. 12. Bright field TEM images for 800°C quenched (a) and (b) furnace cooled 0.75BF-0.25BT samples.$^{62}$

Fig. 13. Backscattered electron (BSE) images of polished surfaces for Bi(Zn$_{2/3}$Nb$_{1/3}$)O$_3$ (BZN) doped BF-BT: (a) BF-BT, (b) BF-BT-0.02BZN, and (c) BF-BT-0.05BZN. EDS elemental mapping results of polished BF-BT-0.05BZN samples: (d) Ba, (e) Ti, (f) Bi, (g) Fe, (h) O, (i) Zn, (j) Nb, and (k) elemental layered image.$^{58}$
quenching could effectively reduce inhomogeneity and increase polarization and strain, as shown in Figs. 15 and 16. They concluded that the major influence was the onset of immiscibility on cooling from the sintering temperature, driven by the electronegativity difference of the dopant species. Effectively, the more covalent the dopants are, the greater the tendency for immiscibility. Calisir et al. studied La-doped BF-BT and they found that isovalent doping promoted solubility and led to a relatively homogeneous microstructure, while donor doping reduced solubility and caused chemical heterogeneity.

6. Piezoelectric Properties

6.1. Dopant and piezoelectric properties

One of the biggest concerns with BiFeO₃ containing systems is the high leakage current arising from either the loss of Bi or from the formation of Fe²⁺ as opposed to Fe³⁺ during sintering. In each case, oxygen vacancies (Vₒ) are generated. To resolve these issues in BF-BT, excess Bi₂O₃ is added to compensate for volatilisation and/or dopants are used to accommodate changes in local defect chemistry associated with the multiple valence state of Fe. Dopants in the field of piezoelectric materials are classified into three groups: donor (higher valence), acceptor (lower valence) and self-compensated (average valence number remains the same). Donor dopants, such as Nb, Mn, are often reported to effectively increase the resistivity of BF-BT (Fig. 17). Zhou et al. reported that Al³⁺ promoted...
the coexistence of \( R \) and \( O \) phases in \( 0.725\text{BiFe}_{1-x}\text{Al}_{x}\text{O}_{3}-0.275\text{BaTiO}_{3} + 1 \text{mol\% MnO}_2 \) ceramics (BFA\(x\)-BT, Table 1) and improved \( d_{33} \) from 126 pC/N \((x = 0)\) to 138 pC/N \((x = 0.01)\). Zhou et al.\(^{86}\) in a further study suggested that for \(0.71\text{BiFe}_{1-x} (\text{Ni}_{1/2}\text{Ti}_{1/2})_x \text{O}_3-0.29\text{BaTiO}_3 + 0.6 \text{wt\% MnO}_2 \) ceramics (BFNT\(x\)-BT), \( x = 0.03 \) had the highest \( d_{33} = 156 \text{pC/N} \) and subsequently reported that \(0.71\text{BiFe}_{1-x} \text{Co}_x \text{O}_3-0.29\text{BaTiO}_3 + 0.6 \text{wt\% MnO}_2 \) (BFC\(x\)-BT) with \( d_{33} = 167 \text{pC/N} \)^{87} in which the grain size was largest, as shown in Fig. 18. Luo et al.\(^{88}\) reported the piezoelectric properties for both A and B site doped BF-BT, \((0.75-BF-0.25-BT-0.05-BMN)\) ceramics.\(^{88}\) in which they described a phase boundary consisting of \(R\) and \(O\) phases \((0.01 \leq x \leq 0.03)\) with \(d_{33} = 108 \text{pC/N} \((x = 0.02)\), as shown in Fig. 19. As evidenced in the brief literature presented above, doped BF-BT ceramics exhibit coexistence of crystal structures (usually \(R\) and \(C\)), which are reputed to give rise to a large piezoelectric response but there are only Murakami et al.\(^{95}\) have proposed crystallochemical trends to optimize dopants based on tolerance factor and electronegativity difference.

Quenching has been frequently used to improve the ferroelectric/piezoelectric properties of BF-BT based compositions, purportedly due to a reduction in the concentration of defects.\(^{54,}^{56,}^{62,}^{91-99}\) Lee et al.\(^{54}\) reported a \(R-T\) MPB in quenched pure BF-BT and Ga/Bi(\(Zn_{0.5}Ti_{0.5}\))O\(3\) (BZT) doped...
BF-BT with the highest \(d_{33}\) values (240–402 pC/N) (Fig. 20) to date. So far these results have not been reproduced by other researchers and typically much smaller values of \(d_{33}\) are reported, e.g., 160–200 pC/N by Zheng et al.\(^91\)–\(^97\) Fig. 21. Kim et al.\(^62\) found the cooling rate during quenching had a significant effect on phase transitions and ferroelectric/piezoelectric properties for BF-BT, as shown in Fig. 22. Wada et al.\(^98\),\(^99\) studied the effect of annealing and quenching on the crystal structure and properties for BF-BT and they ascribed the enhancement of ferroelectric/piezoelectric properties to the domain wall de-pinning and the relaxation of lattice strain induced in the samples after heat treatment (Fig. 23). Quenched samples are thus reported to have useful values of \(d_{33}\) coupled with a high \(T_C\). Although it is feasible that sensors could be fabricated from quenched compositions, it is highly unlikely that high strain monolithic actuators or bimorphs can be fabricated in this manner. Moreover, the formation of reliable multilayer actuators (MLAs) is difficult to rationalize given the differential thermal expansion between the electrode and ceramic layers.

### 6.2. Compositions with high effective \(d_{33}^*\)

In addition to \(d_{33}\), large electric-field induced strain (\(S\)) and \(d_{33}^*\) and low strain hysteresis (SH) are important for actuator applications. Typical, field-induced bipolar and unipolar strain (\(S\)-\(E\)) curves of ferroelectrics are given in Fig. 24. Electric-field-induced positive strain (\(S_{\text{pos}}\)), negative strain (\(S_{\text{neg}}\)) and peak to peak strain (\(S_{\text{pp}}\)) are obtained from the butterfly-shaped bipolar \(S\)-\(E\) loops (Fig. 24(a)).

### Table 1. Lattice parameters (a, b, c and V) and fitting parameters (\(R_{wp}\) and \(S\)) of the 0.725BiFe\(_{1-x}\)Co\(_x\)O\(_4\)–0.275BaTiO\(_3\) + 1 mol% MnO\(_2\) ceramics (BFC\(_x\)-BT) sintered at 970 °C for 2 h.\(^84\)

| \(x\) | \(a (\text{Å})\) | \(b (\text{Å})\) | \(c (\text{Å})\) | \(V (\text{Å}^3)\) | Weight (%) | \(R_{wp}\) | \(S\) |
|------|-------------|-------------|-------------|---------------|------------|---------|-----|
| 0    | 5.6456(6)   | 5.6456(6)   | 13.8615(4)   | 382.2023      | 8.11       | 1.73    |
| 0.01 | 5.6352(2)\(^R\) | 5.6352(2)\(^R\) | 13.8959(6)\(^R\) | 382.157\(^R\) | 80.68      | 1.81    |
| 0.02 | 5.6368(2)\(^R\) | 5.6368(2)\(^R\) | 13.8726(8)\(^R\) | 381.732\(^R\) | 75.63      | 1.43    |
| 0.03 | 5.6338(6)\(^R\) | 5.6338(6)\(^R\) | 13.8844(9)\(^R\) | 381.6566\(^R\) | 45.35      | 1.58    |
| 0.04 | 5.6391(9)\(^O\) | 5.6475(3)\(^O\) | 5.6440(6)\(^O\) | 127.2437      | 8.2        | 1.74    |
| 0.05 | 5.6934(5)\(^O\) | 5.6435(5)\(^O\) | 5.6421(2)\(^O\) | 127.1583      | 8.12       | 1.74    |
| 0.06 | 5.9954(5)\(^O\) | 5.6654(3)\(^O\) | 5.6350(4)\(^O\) | 127.1292      | 8.8        | 1.74    |
| 0.07 | 5.9985(3)\(^O\) | 5.6340(6)\(^O\) | 5.6447(6)\(^O\) | 127.1652      | 9.6        | 1.54    |
| 0.08 | 5.9980(4)\(^O\) | 5.6393(5)\(^O\) | 5.6407(9)\(^O\) | 127.1794      | 9.2        | 1.61    |

Fig. 18. (a) SEM images and (b) \(d_{33}\) and planar electromechanical coupling factor \(k_p\) of 0.71BiFe\(_{1-x}\)Co\(_x\)O\(_4\)-0.29BaTiO\(_3\)+0.6 wt% MnO\(_2\) (BFC\(_x\)-BT) ceramics.\(^87\)
\[ d_{33}^{\prime} = S_{\text{max}} / E_{\text{max}}; \quad (1) \]
\[ \text{SH} = H_{\text{max}} / S_{\text{max}}; \quad (2) \]

where \( S_{\text{max}}, E_{\text{max}} \) and \( H_{\text{max}} / S_{\text{max}} \) is the average electric-field-induced maximum strain obtained from the unipolar S-E loops, the maximum electric field and the width of the loop at half the applied field, respectively, as shown in Fig. 24(b).

Undoped BF-BT at the R to C phase boundary have a value of \( d_{33}^{\prime} \) below 100 pm/V, mainly due to their high conductivity.\(^5\) Leontsev et al.\(^5\) found Mn improved the DC resistivity by 1 \( \sim \) 5 orders of magnitude and increased \( d_{33}^{\prime} \) up to 331 pm/V with \( S_{\text{max}} = 0.166\% \) (Table 2). Wang et al.\(^5\) doped Nd and BZN into BF-BT and obtained \( S_{\text{pos}} \sim 0.463\% \) and \( d_{33}^{\prime} \sim 424 \text{ pm/V} \) with SH of 37\% for 0.5\%BZN doped BF-BT (Fig. 25). The origin of the large strain was ascribed to a field-induced transition from short- to long-range dipolar order at the crossover from normal to a relaxor ferroelectric behavior. High \( S_{\text{max}} \) of 0.4\% with large \( d_{33}^{\prime} \sim 544 \text{ pm/V} \) was achieved in BMN doped BF-BT by Murakami et al.,\(^5\) as shown in Fig. 26, who also suggested that \( S_{\text{max}} \) and \( d_{33}^{\prime} \) was optimized at the point of crossover from relaxor to ferroelectric which facilitates a macroscopic field induced transition to a ferroelectric state. The same authors fabricated a prototype MLA based on the composition 0.63BF-0.32BT-0.05BMN\(^5\) which gave a displacement of \( \sim 1.5 \mu \text{m} \) at 7 kV/mm, as shown in Fig. 27. Importantly, the high strains reported by Murakami et al.\(^5\)–\(^8\) were achieved in ceramics and MLAs that were furnace cooled and hence might be considered more promising for commercial applications.

In contrast to Murakami et al. quenched BF-BT and Ga/BZT doped BF-BT were reported with high values of

Fig. 19. Variations of (a) \( d_{33} \) and \( k_p \), (b) \( \varepsilon_r \) and \( \tan \delta \); (c) Lattice parameters \( a, b, c, \) and \( V \) of \((0.75-x)\text{BiFeO}_3-0.25\text{BaTiO}_3-x\text{La}(Co_{0.5}\text{Mn}_{0.5})\text{O}_3+1 \text{ mol\% MnO}_2 \) (BF-BT-xLCM) ceramics as a function of \( x \).\(^8\)

Fig. 20. (a) \( d_{33} \) (filled symbols) and \( d_{33}^{\prime} \) (empty symbols) values of the BF-BT, BF-BT-3BZT, and BF-BT-3BG ceramics as functions of BT content. (b) Comparison of \( d_{33} \) among other lead-free piezoelectrics and PZT family.\(^5\)}
$d_33 = 375 \approx 410 \text{ pm/V}$ with $S_{\text{max}}$ of $0.15 \sim 0.225\%$ by Lee et al. (Fig. 20), but these authors attributed the large electromechanical response to coexisting $R$ and $T$ phases at MPB. Ryu et al. prepared BZT and LN doped BF-BT by quenching process and high $d_33$ of 600 pm/V was obtained at 30 kV/cm with SH of 38% (Fig. 28). These authors believed the high strain mainly came from the enhancement of domain wall density and mobility under the applied electric field. However, Wada et al. investigated the effect of electric field on the phase structure and piezoelectric response for both pure BF-BT and Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ (BMT) doped BF-BT by in-situ synchrotron radiation X-ray diffraction (SR-XRD). No peak splitting was observed in the diffraction peaks (Fig. 29) and they concluded that there was no electric-field-induced phase transition either in BF-BT nor BMT doped BF-BT ceramics.

Table 3 summaries results of BF-BT ceramics with the composition, the dopant, the sintering method, the piezoelectric properties and the $T_C$ (the maximum dielectric permittivity ($T_m$) optimized. Optimized compositions fluctuate from 0.67BF-0.33BT to 0.75BF-0.25BT and $d_33$ varies from 100 to 200 pC/N. The highest $d_33$ reported to date is 402 pC/N for quenched 3 mol% Ga-doped 0.67BF-0.33BT but in this context appears anomalously high. $d_33$ values are in the range of 128 $\sim 600$ pm/V and consistently higher than $d_33$. $d_33$ appears reproducible in so much as large value of strain can be routinely achieved, albeit at high fields ($> 5$ kV/cm). Given the complexity of the phase assemblage, microstructure and structure in the BF-BT system, a generalized overview of the crystal chemistry is difficult. However, the low $d_33$ and absence of a $T$ phase of similar free energy to $R$ ($C$ coexists with $R$ phases according to most authors) also points to nonclassic MPB behavior. A more rational explanation of the dominant electrostrictive behavior is the growth of a long-range ferroelectric phase from relaxor-like nano-domains. The absence of $T$ phase in the vicinity of optimized composition, suggests
Fig. 23. Structural properties of BF-0.2BT_V, BF-0.2BT_A, and BF-0.2BT_Q. (a) Williamson Hall analysis; (b) Lattice constants and rhombohedral distortion (90-α); (c) A-O and B-O bond-length.⁹⁹

Fig. 24. The schematic figure of the field-induced (a) bipolar and (b) unipolar S-E curves of ferroelectrics.
that the ferroelectric phase is most likely \( R \) and thus peak splitting is difficult to observe in \textit{in-situ} studies.\textsuperscript{100,101} This model however, requires further verification through \textit{in-situ} studies that focus on determining the structure of the field induced state. Structural refinements however, are complicated by the core-shell microstructure often reported in undoped and doped compositions, and we recommend that future investigations are carried out on chemically homogeneous samples (by BSE images) such as those described by Murakami \textit{et al.}\textsuperscript{56,57}

A comparison of \( d_{33} \) versus \( T_C/T_m \), \( d_{33}^* \) versus \( T_C/T_m \) and \( S_{\text{max}} \) versus \( d_{33}^* \) for lead-based and lead-free piezoelectric ceramics is plotted in Fig. 30.\textsuperscript{10–138} Generally, the values of \( d_{33}^*/d_{33} \) decrease with the increase of \( T_C/T_m \), but lead-based ceramics still exhibit larger \( d_{33}^*/d_{33} \) values compared to lead-free ceramics (Figs. 30(a) and 30(b)). In addition, some doped BF-BT ceramics exhibit high values of \( S_{\text{max}} > 0.4\% \) amongst ferroelectric ceramics (Fig. 30(c)), with \( d_{33}^*/C_{33} > 400 \text{ pm/V} \) and \( SH < 40\% \).

### 7. Energy Storage Property

Dielectric capacitors are attractive for high-voltage pulse power application due to their high energy density and fast charge-discharge rate\textsuperscript{139–142} with linear dielectrics (LD), antiferroelectrics (AFE) and relaxor-ferroelectrics (RFE) all considered excellent candidates. Energy density \( W \) for LD

\[
W = \frac{1}{2} CV^2
\]

where \( C \) is the capacitance and \( V \) is the voltage. The energy density is given by the area under the \( P-E \) or \( S-E \) loops, as shown in Fig. 25(a) and (b).

![Fig. 25. High electric field (a) bipolar P-E, (b) bipolar S-E and (c) unipolar S-E loops of Bi(Zn\textsubscript{2/3}Nb\textsubscript{1/3})O\textsubscript{3} (BZN) doped BF-BT (BF-BT-xBZN) samples at 100 kV/cm. (d) \( P_r \) and \( E_C \) as a function of BZN concentration. (e) \( S_{\text{pos}} \) and \( S_{\text{neg}} \) as a function of BZN concentration. (f) \( d_{33}^* \) and SH as a function of BZN concentration. \( d_{33} \) as a function of BZN concentration is in the inset of (d).\textsuperscript{58}](image-url)
Fig. 25. (Continued)

(a) Unipolar $S$-$E$ curves; (b) $d_{33}^{\pm}$ and $d_{33}'$ of unpoled Bi(Mg$_{2/3}$Nb$_{1/3}$)O$_3$ (BMN) doped BF-BT (BT-xBF-BMN, $x = 0.55, 0.60, 0.63, 0.65, 0.70, \text{and} 0.75$) ceramics.\textsuperscript{56}

Fig. 26. (a) Unipolar $S$-$E$ curves; (b) $d_{33}^{\pm}$ and $d_{33}'$ of unpoled Bi(Mg$_{2/3}$Nb$_{1/3}$)O$_3$ (BMN) doped BF-BT (BT-xBF-BMN, $x = 0.55, 0.60, 0.63, 0.65, 0.70, \text{and} 0.75$) ceramics.\textsuperscript{56}
Fig. 27. (a) Cross-sectional SEM image of a Bi(Mg$_{2/3}$Nb$_{1/3}$)O$_3$ (BMN) doped BF-BT (0.63BF-0.32BT-0.05BMN) multilayer actuator; (b) $P$-$E$ loop and displacement-electric field ($D$-$E$) curve.

Fig. 28. Piezoelectric response of Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ (BZT)-modified BF-BT (BF-BT-xBZT) ceramics (a) $d_{33}$ and $d_{33}^*$ under 30 kV/cm; (b) $d_{33}^*$ of BF-BT-0.02BZT ceramics as a function of different applied fields. Inset shows field-induced strain at 30 kV/cm.

Fig. 29. The in-situ synchrotron radiation X-ray diffraction (SR-XRD) patterns of 0.67BF-0.33BT ceramics under the electric field with selected 2θ angles (a) from 7.1°–7.3° for (110), (b) from 8.7°–8.9° for (111), and (c) from 10.1°–10.3° for (200), respectively.
is calculated using Eq. (3):

\[
W = \frac{1}{2}DE = 1/2\varepsilon_0\varepsilon_eE^2, \tag{3}
\]

where \( D \) is the electrical displacement, \( E \) is the electric field, \( \varepsilon_0 \) and \( \varepsilon_e \) are the permittivity of free space and relative permittivity, respectively. Large values of \( W \) are obtained with both high \( \varepsilon_e \) and \( E \) for LD. For nonlinear dielectrics, the \( P-E \) loop is commonly used to calculate energy storage performance, as shown schematically in Fig. 31. The total energy density \( (W) \), recoverable energy density \( (W_{\text{rec}}) \) and energy conversion efficiency \( (\eta) \) are:

\[
W = \int_0^{P_{\text{max}}} EdP, \tag{4}
\]

\[
W_{\text{rec}} = \int_{P_{\text{r}}}^{P_{\text{max}}} EdP, \tag{5}
\]

\[
\eta = \frac{W_{\text{rec}}}{W}. \tag{6}
\]

To obtain high \( W_{\text{rec}} \) and \( \eta \), high \( P_{\text{max}} \), low \( P_r \) and high breakdown strength \( (E_{\text{BDS}}) \) are essential. AFE and RFE are anticipated to display optimum \( W_{\text{rec}} \) and \( \eta \) since both exhibit high \( \Delta P \) \( (P_{\text{max}} - P_r) \) and \( E_{\text{BDS}} \) values. Undoped BF-BT is a FE with high \( P_r \) and hysteresis but low \( \Delta P \) and \( E_{\text{BDS}} \) and thus not suitable for energy storage. To decrease \( P_r \)/hysteresis and increase \( \Delta P/E_{\text{BDS}} \), dopants may be substituted into the BF-BT solid solution in a deliberate attempt to force the phase transition from ferroelectric to relaxor.

### 7.1. A or B site doping

Slight \( P-E \) loops were observed by Calisir et al.\textsuperscript{54} in 0.75BiFeO\textsubscript{3}-0.25(Ba\textsubscript{0.98}La\textsubscript{0.02})\textsubscript{5}Ti\textsubscript{3}O\textsubscript{15} (BF-BLT) ceramics, exhibiting high \( P_{\text{max}} \approx 0.15 \text{ C/m}^2 \) and low \( P_r \approx 0.04 \text{ C/m}^2 \) with \( W_{\text{rec}} \approx 0.61 \text{ J/cm}^3 \) (Fig. 32). Double switching peaks were observed in \( J-E \) loop (Fig. 32(a)), indicating a reversible switching between an ergodic-relaxor (ER) and metastable

| Composition | Sintering method | \( d_{33} \) (pC/N) | \( d_{33} \) (pm/V) | \( S_{\text{max}} \) (%) | \( T_c/T_m \) (ºC) | Ref. |
|-------------|-----------------|---------------------|---------------------|-------------------------|----------------------|----|
| 0.75BF-0.25BT | Furnace cooled | 47 | 128 | 0.064 | 574 | 53 |
| 0.67BF-0.33BT | Furnace cooled | 33 | 151 | 0.0755 | 605 | 55 |
| 0.75BF-0.25BT + Mn | Furnace cooled | 116 | 142 | 0.071 | 619 | 53 |
| 0.68BF-0.31BT + Mn | Furnace cooled | 82 | 331 | 0.1655 | 598 | 53 |
| 0.67BF-0.33BT + Mn | Furnace cooled | 70 | 327 | 0.1635 | 605 | 53 |
| 0.67BF-0.33BT + Mn | Furnace cooled | 43 | 306 | 0.153 | 580 | 53 |
| 0.75BF-0.25BT + Mn | Furnace cooled | 120 | 127 | 0.089 | 522 | 61 |
| 0.75BF_{0.97}La_{0.03}F-0.25BT + Mn | Furnace cooled | 140 | 144 | 0.101 | 490 | 61 |
| 0.75BF_{0.95}Nd_{0.05}F-0.25BT + Mn | Furnace cooled | 120 | 200 | 0.14 | 379 | 61 |
| 0.7BF-0.3BT + Mn | Furnace cooled | 190 | 240 | 0.144 | 478 | 83 |
| 0.7BF_{0.98}Nd_{0.02}F-0.3BT + Mn | Furnace cooled | 50 | 333 | 0.2 | 390 | 83 |
| 0.725BF_{0.96}Sc_{0.04}F-0.275BT + Mn | Furnace cooled | 143 | / | / | 596 | 74 |
| 0.7BF_{0.98}La_{0.02}F-0.29BT + Mn | Furnace cooled | 168 | / | / | 400 | 80 |
| 0.7BF-0.25BT-0.05BiScO\textsubscript{3} | Furnace cooled | 145 | 465 | 0.233 | 400 | 57 |
| 0.72BF_{0.96}Al_{0.04}F-0.28BT | Furnace cooled | 123 | / | / | 450 | 84 |
| 0.7BF-0.25BT-0.02LCM + Mn | Furnace cooled | 108 | / | / | 523 | 88 |
| 0.7BF_{0.98}Co_{0.02}F-0.29BT + Mn | Furnace cooled | 167 | / | / | 488 | 87 |
| 0.65BF-0.3BT-0.05BZT + Mn | Furnace cooled | 139 | / | / | 523 | 89 |
| 0.695BFF-0.3BT-0.05BZN + Mn | Furnace cooled | 160 | 424 | 0.463 | 480 | 58 |
| 0.7BF_{0.97}Ni_{0.03}Ti_{2/3}O_{5/3}F-0.29BT | Furnace cooled | 156 | / | / | 431 | 86 |
| 0.725BF-0.25BT-0.1025BT + Mn | Furnace cooled | 135 | / | / | 708/544 | 65 |
| B_{1.62}F_{0.96}Mg_{0.02}Ti_{0.02}O_{3}F-0.3BT | Furnace cooled | 198 | / | / | 497 | 73 |
| 0.7BF-0.25BT-0.05BNN | Furnace cooled | 148 | 410 | 0.41 | 450 | 56 |
| 0.63BF-0.32BT-0.05BNN | Furnace cooled | 20 | 544 | 0.272 | 380 | 56 |
| 0.715BF-0.275BT-0.01BNN + Mn | Furnace cooled | 140 | / | / | 560 | 90 |
| 0.6BF-0.3BT-0.01BNN + Mn | Furnace cooled | 94 | 189 | 0.0945 | 470 | 98 |
| 0.7B_{1.07}F-0.3BT | Quenched | 180 | / | / | 506 | 71 |
| 0.7B_{1.05}F_{0.97}Sc_{0.03}F-0.3BT | Quenched | 180 | / | / | 500 | 91 |
| 0.7BF-0.3BT + 1 mol%Bi\textsubscript{2}O\textsubscript{3} | Quenched | 200 | 333 | 0.1 | 500 | 92 |
| 0.7BF-0.3BT + 0.5 mol%CuO | Quenched | 165 | 449 | 0.2694 | 503 | 94 |
| 0.7BF-0.29BT + 0.3 mol%Mn\textsubscript{2}O\textsubscript{3} | Quenched | 191 | / | / | 530 | 95 |
| 0.60BF-0.40BT-0.02BZT | Quenched | 50 | 600 | 0.18 | 350 | 93 |
| 0.90(0.67BF-0.33BT)F-0.01LN | Quenched | 146 | 500 | 0.175 | 390 | 97 |
| 0.69BF_{0.95}F-0.3BT-0.03BZT | Quenched | 195 | 200 | 0.13 | 505 | 96 |
| 0.67BF-0.3BT | Quenched | 240 | 270 | 0.15 | 456 | 54 |
| 0.64BF_{1.05}F-0.33T-0.03BZN | Quenched | 324 | 345 | 0.19 | 466 | 54 |
| 0.67BF_{1.05}F_{0.95}Gd_{0.05}F-0.33T | Quenched | 402 | 410 | 0.225 | 454 | 54 |
FE states. Wang et al.\textsuperscript{61} reported slim $P$-$E$ loops, enhanced $E_{\text{BDS}}$ and high $\Delta P$ in Nd doped BF-BT (Figs. 33 and 34), which they attributed to a phase transition to a RFE phase, enhanced density and reduced grain size, as shown in Fig. 35. High $W_{\text{rec}} \sim 1.82$ J cm$^{-3}$ and $\eta \sim 87.8\%$ were obtained for 15\% and 40\% Nd-doped 0.7BF-0.3BT (BN15F-BT and BF40F-BT), respectively, Fig. 36. Multilayers (MLs) of BN15F-BT were fabricated with an exceptional high value of $W_{\text{rec}} \sim 6.74$ J cm$^{-3}$ with $\eta \sim 77\%$ obtained under an electric field of 540 kV/cm, which exhibited good temperature stability $< 15\%$ up to 125$^\circ$C, Fig. 37.\textsuperscript{61} Beside lanthanide doping on the A site, Nb$^{5+}$ on the B-site was substituted in 0.65BF-0.35BT which resulted in $P_r \sim 5 \mu C/cm^2$ but a less impressive $W_{\text{rec}} \sim 0.71$ J/cm$^3$.\textsuperscript{143}

7.2. $\text{ABO}_3$ substitutions

Other than utilizing direct A or B site doping, the formation of ternary solid solutions by the addition of a third $\text{ABO}_3$
Fig. 32. (a) $P$-$E$ and $J$-$E$ loops; (b) energy density properties for $0.75\text{BiFeO}_3$-$0.25(\text{Ba}_{0.99}\text{La}_{0.01})\text{TiO}_3$ (BF-BLT).

Fig. 33. Unipolar $P$-$E$ loops under different electric fields for Nd doped $0.75\text{BiFeO}_3$-$0.25\text{BT}$ ($\text{BN100x}\text{F-BT}$) (a) BN15F-BT, (b) BN20F-BT, (c) BN30F-BT and (d) BN40F-BT.
compound have been used to enhance energy storage properties. Zheng et al.\textsuperscript{144} reported high $W_{\text{rec}}/C_{24}$: 56 J/cm$^3$ with $\eta_{\text{C}24}$/75$\%$ under an electric field of 12.5 kV/mm in Ba\(_{(Mg^{1/3}Nb^{2/3})O_3}\) (BMN) doped BF-BT solid solution, as shown in Fig. 38, which had a good temperature stability from 25 to 190$^\circ$C (Figs. 38(b) and 38(d)). They also found similar energy storage properties ($W_{\text{rec}}$ ~ 1.66 J cm$^{-3}$ with $\eta$ ~ 82$\%$) in 0.61BF-0.33BT-0.06La\(_{(Mg^{1/2}Ti^{1/2})O_3}\) (BF-BT-0.06LMT), Fig. 39.\textsuperscript{145} Liu et al. recently reported 0.06Sr\(_{(Al^{0.5}Nb^{0.5})O_3}\) (SAN)-0.6BF-0.34BT compositions with slim

Fig. 34. $P_{\text{max}}$, $P_r$ and $\Delta P$ as a function of electric field for Nd doped 0.75BF-0.25BT (BN100xF-BT) (a) BN15F-BT, (b) BN20F-BT, (c) BN30F-BT and (d) BN40F-BT; $P_{\text{max}}$, $P_r$ and $\Delta P$ as a function of Nd concentration at 170 kV/cm are shown in the inset of (d).\textsuperscript{61}

Fig. 35. (a) XRD patterns of Nd doped 0.75BF-0.25BT (BN100xF-BT); (b) average grain size and relative density of BN100xF-BT as a function of Nd concentration.\textsuperscript{61}
Fig. 36. (a) $W$, (b) $W_{rec}$ and (c) $\eta$ of Nd doped 0.75BF-0.25BT (BN100xF-BT): BN15F-BT, BN20F-BT, BN30F-BT and BN40F-BT as a function of electric field; (d) $W$, $W_{rec}$ and $\eta$ as a function of Nd concentration at 170 kV/cm.61

Fig. 37. (a) Unipolar $P$-$E$ loops of BN15F-BT MLs under different electric fields at RT, (b) in-situ temperature dependence of unipolar $P$-$E$ loops of MLs at an electric field of 300 kV/cm, (c) $W$, $W_{rec}$ and $\eta$ of MLs as a function of electric field at RT, and (d) $W$, $W_{rec}$ and $\eta$ of MLs as a function of temperature at 300 kV/cm; SEM image of MLs is in the inset of (a).61
Fig. 38.  P-E loops under different (a) electric fields and (b) temperature for 0.06Ba(Mg_{1/3}Nb_{2/3})O_3 (BMN) doped BF-BT (BF-BT-0.06BMN) ceramic, and both $W$ and $\eta$ values as a function of (c) electric field and (d) temperature.\textsuperscript{144}
P-E loops, $W_{rec} \sim 1.75 \text{ J/cm}^3$ and $\eta \sim 66\%$ at 15.5 kV/mm, as shown in Figs. 40(a) and 40(b),\textsuperscript{146} with thermal stability from 30–120°C (Figs. 40(c) and 40(d)).

7.3. Control of microstructure through doping

The microstructural features in dielectric ceramics play an essential role on $E_{BDS}$, including porosity, grain boundary, inhomogeneity, second phase and grain size. The following relationship between $E_{BDS}$ and average grain size ($G$) was proposed by Tunkasiri et al.,\textsuperscript{147} confirming that smaller $G$ leads to higher $E_{BDS}$:

$$E_{BDS} \propto \frac{1}{\sqrt{G}}.$$  \hspace{1cm} (7)

Fig. 39. (a) $P$-$E$ loops and (b) $W$ for La(Mg\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3} (LMT) doped BF-BT (BF-BT-xLMT) ceramics with different x concentration.\textsuperscript{145}

Fig. 40. Unipolar $P$-$E$ loops under different (a) electric fields and (c) temperature for 0.06Sr(Al\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3} (SAN) doped BF-BT (0.6BF-0.34BT-0.06SAN) and $W$, $W_{rec}$, and $\eta$ as a function (b) electric field and (d) temperature.\textsuperscript{146}
In most cases, $G$ reduces with increasing dopant concentration with a commensurate improvement in $E_{\text{BDS}}$. $E_{\text{BDS}}$ of dielectric ceramics is also greatly increased with a reduction in porosity and defects.\textsuperscript{148,149} For example, a large $G$ of ~7\,\mu m was observed in undoped 0.7BF-0.3BT ceramics (Fig. 35(b)) normally breaks down at 100\,kV/cm.\textsuperscript{58,61,83} With addition of dopants, such as Nd\textsuperscript{3+} reported by Wang et al.\textsuperscript{61} a significant reduction of both $G$ (1–2\,\mu m) and porosity was

![Graph](image)

Fig. 41. Unipolar $P$-$E$ loops under different electric fields for Bi(Zn\textsubscript{2/3}Nb\textsubscript{1/3})O\textsubscript{3} (BZN) doped BF-BT (BF-BT-xBZN) (a) BF-BT-0.05BZN and (b) BF-BT-0.08BZN. $W$, $W_{\text{rec}}$, and \eta as a function of electric field for (c) BF-BT-0.05BZN and (d) BF-BT-0.08BZN.\textsuperscript{58}

In most cases, $G$ reduces with increasing dopant concentration with a commensurate improvement in $E_{\text{BDS}}$. $E_{\text{BDS}}$ of dielectric ceramics is also greatly increased with a reduction in porosity and defects.\textsuperscript{148,149} For example, a large $G$ of ~7\,\mu m was observed in undoped 0.7BF-0.3BT ceramics (Fig. 35(b)) normally breaks down at 100\,kV/cm.\textsuperscript{58,61,83} With addition of dopants, such as Nd\textsuperscript{3+} reported by Wang et al.\textsuperscript{61} a significant reduction of both $G$ (1–2\,\mu m) and porosity was

| Compounds | $E$ (kV/cm) | $W$ (J/cm$^3$) | $W_{\text{rec}}$ (J/cm$^3$) | \eta (%) | Ref. |
|-----------|-------------|----------------|----------------|---------|-----|
| 0.97(0.65BF-0.35BT-0.03Nb | 90 | / | 0.71 | / | 143 |
| 0.75BF-0.25B$_{0.05}$La$_{0.01}$T | 100 | / | 0.61 | / | 64 |
| 0.75B$_{0.35}$Nd$_{0.15}$F-0.25BT | 170 | 4.1 | 1.82 | 41.3 | 61 |
| 0.75B$_{0.35}$Nd$_{0.15}$F-0.25BT | 180 | 0.75 | 0.66 | 87.8 | 61 |
| 0.61BF-0.33BT-0.06BMN | 125 | 2.08 | 1.56 | 75 | 144 |
| 0.61BF-0.33BT-0.06LMT | 130 | 2.02 | 1.66 | 82 | 145 |
| 0.68BF-0.34BT-0.06SAN | 155 | 2.69 | 1.75 | 65 | 146 |
| 0.65BF-0.3BT-0.05BZN | 180 | 3.7 | 2.06 | 53 | 58 |
| 0.65BF-0.3BT-0.08BZN | 190 | 2.9 | 1.98 | 68 | 58 |
| BF-BT multilayers | 540 | 8.75 | 6.74 | 77 | 61 |

Table 4. Summary of the energy storage properties for reported BF-BT ceramics. (BMN = Ba(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}, LMT = La(Mg\textsubscript{1/2}Ti\textsubscript{1/2})O\textsubscript{3}, BZN = Bi(Zn\textsubscript{2/3}Nb\textsubscript{1/3})O\textsubscript{3}, SAN = Sr(Al\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3}).
achieved by Nd doping (Fig. 35(b)), increasing $E_{\text{BDS}}$ (180–190 kV/cm), resulting in an improvement of $W \sim 4.1 \text{J/cm}^3$ and $W_{\text{rec}} \sim 1.82 \text{J/cm}^3$, as shown in Fig. 36.

Additionally, as discussed in Sec. 5.1, compositional inhomogeneity with core-shell microstructure is often observed in doped BF-BT ceramics. However, this is not considered detrimental to energy storage behavior. $W_{\text{rec}} \sim 2.1 \text{J/cm}^3$ and $\eta \sim 53\%$ under an electric field of $\sim 180 \text{kV/cm}$ was reported in core-shell 0.65BF-0.3BT-0.05BZN compositions (Figs. 13, 14 and 41)\textsuperscript{58} which they attributed to slim $P$-$E$ loops.

The energy storage properties for reported BF-BT ceramics and MLs are summarized in Table 4 and the comparison of energy-storage properties among lead-based and lead-free ceramics/capacitors (a) $W_{\text{rec}}$ versus electric field and (b) $\eta$ versus $W_{\text{rec}}$\textsuperscript{58,61,64,143–194}

Among all reported BF-BT ceramics, 0.05BZN and 0.4Nd doped BF-BT exhibits the highest values of $W_{\text{rec}} \sim 2.1 \text{J/cm}^3$ and $\eta \sim 87.8\%$, respectively (Table 4). Compared with lead-based and other lead-free ceramics, as shown in Fig. 42, the values of $W_{\text{rec}}$ for BF-BT ceramics are promising but antiferroelectrics (AFE, PLZT, AgNbO$_3$, some BNT-based ceramics) are higher. Authors however, do not often report the concomitant large strain associated with AFE/FE transitions which may prove detrimental to the longevity of a device in service due to mechanical fatigue during charge discharge.\textsuperscript{194} Nd-doped BF-BT MLs exhibit the largest $W_{\text{rec}} \sim 6.74 \text{J cm}^{-3}$ with high $\eta \sim 77\%$ in BF-BT based systems but we note that recent unpublished data by the present authors have now surpassed these values with $W_{\text{rec}} > 10 \text{J/cm}^3$. This latter value exceeds that reported by Li et al.\textsuperscript{194} for (Bi,Sr)TiO$_3$ doped NBT MLs ($> 9 \text{J/cm}^3$).

In summary, the methodologies for developing high energy density materials are now known and BF-BT compositions can be readily adapted to have high $E_{\text{BDS}}$ and large $\Delta P$. The role of dopants/third end member in the solid solution is many fold. The dopants decrease $P_r$, increase $E_{\text{BDS}}$ through improved density, decreased grain size and possibly inducing a core-shell microstructure. Multilayering compositions further increases $E_{\text{BDS}}$ and improves the $\eta$ with respect to bulk performance. We encourage researchers to explore the compositional design space that this methodology permits to improve the performance of BF-BT systems with $W_{\text{rec}} \sim 15 \text{J/cm}^3$ a realistic target. The low strains associated with RFE, BF-BT based MLs offer significant advantages over their AFE counterparts, and work is now required to explore cheaper internal electrode options (current prototypes are fabricated from Pt internal electrodes) to reduce manufacturing costs.

8. BF-BT films

BF-BT films have attracted recent attention for potential applications in ferroelectric random access memory (FeRAM) and microelectromechanical systems (MEMS).\textsuperscript{195–215} Compared with PZT or other lead-free materials, only few studies have focused on BF-BT films. Ueda et al.\textsuperscript{216} prepared BF-0.3BT films by the pulsed-laser deposition technique in 1999, which found coexistence of weak ferroelectricity and ferromagnetism ($P_r \sim 2.5 \mu \text{C/cm}^2$, Fig. 43). Ito et al.\textsuperscript{217} prepared BF-0.3BT films by chemical solution deposition and Mn doping reduced the leakage current, leading to improvement in ferroelectric properties to $P_S \sim 60 \mu \text{C/cm}^2$ and $P_r \sim 27 \mu \text{C/cm}^2$ at a field of 800 kV/cm. Liu et al.\textsuperscript{218} grew BF-xBT films by chemical solution deposition and achieved high values of $P_r \sim 19.7–76.6 \mu \text{C/cm}^2$ at 940 kV/cm. Although there are only a few papers on BF-BT film, Lee et al.\textsuperscript{219} (2016) recently reported that 300 nm thick BF-0.33BT achieved local piezoelectric constant ($d_{33, \text{PFM}}$) of 92.5 pm/V with high $T_C$ of 405$^\circ$C (Fig. 44). In addition, Lee et al.\textsuperscript{219} further compared the temperature dependence of $\varepsilon_r$ between film and bulk of the same composition observing
that the dielectric anomaly of the film was broader than that of the bulk (Figs. 44(b) and 44(c)), due to stress effects relating to the presence of a high volume fraction of grain boundary compared with bulk and differences in thermal expansion between film and substrate. To our knowledge however, there are still no reports on BF-BT films for energy storage. A Mn-doped 0.4BiFeO₃-0.6SrTiO₃ (BF-ST) thin film capacitor was reported by Pan et al.\textsuperscript{220} which achieved

![Image](image-url)

Fig. 44. (a) The local piezoelectric hysteresis loops of electric field dependent strain and $d_{33,PFM}$ of 0.67BF-0.33BT (BF-33BT) thin film; Temperature dependence of $\varepsilon_r$ and dielectric loss ($\tan \delta$) of BF-33BT (b) bulk ceramic and (c) thin film.\textsuperscript{219}
an ultrahigh $W_{\text{rec}} \sim 51 \text{J/cm}^3$ (Fig. 45), superior to other lead-free systems and comparable with the best lead-based films. Similar high energy storage performance in BF-BT films are realistic based on the excellent properties of ceramics and MLs.

9. Further Potential Applications of BF-BT

In comparison to PZT, BF-BT ceramics are in their infancy with significant scientific interest only emerging after the work of Leontiev et al. Since this publication, BF-BT systems have been shown to be suitable for sensor, actuator and energy storage applications. However, there are a number of further attractive features/properties that show promise for other applications. Electrocalorics are required to progress through the Carnot cycle (Fig. 46). The design metrics are low strain to prevent mechanical fatigue, high $E_{\text{BDS}}$ and the ability to induce a large entropy change associated with the large polarization change through the application of cyclic field such as occurs in a field induced relaxor to ferroelectric transition. The ability to form robust multilayers is also an advantage for the fabrication of channelled device structures. It is evident that doped BF-BT compositions meet these criteria and thus should be considered as possible candidates for electrocaloric solid state cooling systems.

Pyroelectricity is the electrical response of an insulating dielectric to a change in temperature, which is found in polar materials with noncentrosymmetric structure. Figures of merit (FOMs) are critical for pyroelectric materials and devices, which could be maximized by high pyroelectric coefficient ($p$, determined by $P_3$) as well as both low values of $\varepsilon_r$ and $\tan \delta$. To our knowledge, the pyroelectric properties of BF-BT systems remain unknown at this time but the ability to manipulate the system though an array of dopants that influence the phase assemblage and the relaxor to ferroelectric behavior suggest that research may yield interesting pyroelectric compositions.

Fig. 45. (a) P-E loops of 0.4BiFeO$_3$-0.6SrTiO$_3$ (BF-ST) film with various applied electric fields at 1 kHz. The inset is the $J$ of BF-ST film at various DC biased electric fields. (b) Stored energy density $U$, recoverable energy density $U_{\text{rec}}$, hysteresis loss $U_{\text{loss}}$, and $\eta$ as a function of the applied electric field.220

Fig. 46. Two half-cycles in Carnot cooler cycle.221
10. Summary and Future Work

(1) Crystal structure and microstructure is critical and can strongly affect the performance of BF-BT ceramics. The optimum piezoelectric properties ($d_{33} = 100 \sim 402 \text{pC/N}$, $d_{33} = 126 \sim 600 \text{pC/N}$) are commonly achieved at the $R-C$ phase boundary. The crystal structure of compositions at this boundary is still ambiguous and further work is required to understand the average and local structure. Specifically, in-situ XRD and TEM is needed to determine the behavior as a function of applied field and temperature.

(2) Compositional inhomogeneity with core-shell microstructure (Ba/Ti-rich shell and Bi/Fe-rich core) have been investigated by EDS, TEM and impedance. Although compositional inhomogeneity is considered harmful to piezoelectric properties, enhanced energy storage property has been observed for core-shell BF-BT-xBZN. Further work is required to understand the role of chemical homogeneity on breakdown strength and polarisation.

(3) Thermal treatment (annealing and quenching) affect the crystal structure have been reported to eliminate compositional inhomogeneity and improve the ferroelectric/piezoelectric properties. Quenched Ga-doped BF-BT ceramics have been reported with mixed $R3c$ and $P4mm$ phases which possess $d_{33} \sim 402 \text{pC/N}$. Large strains are achieved in many compositions and $d_{33}$ is routinely reported to exceed 400 pm/V but to date large conventional $d_{33}$ values have not been reproduced on either furnace cooled or quenched samples. Further studies are required to reproduce this data and assess whether processing methodologies are suitable for scale-up.

(4) A/B site doping and extension of the solid solution with a third end member have proved to be effective in achieving high $P-E$ loops and enhancing $E_{\text{BDS}}$ in the BF-BT system. Multilayering further increases $E_{\text{BDS}}$ and improves $\eta$. We recommend that the outlined methodologies are utilized by researchers to improve iteratively the energy storage properties in the BF-BT system with $W_{\text{rec}} \sim 15 \text{J/cm}^3$ a realistic target.

(5) BF-BT films have been successfully prepared by different methods, including pulsed-laser and chemical solution deposition. The energy storage properties have not been reported in BF-BT films so far but given the high $E_{\text{BDS}}$ of MLs and ceramics and the high $W_{\text{rec}}$ ($\sim 513 \text{J/cm}^3$) reported for BF-ST thin films, we strongly recommend that further studies are carried out.

(6) We note that long term reliability of BF-BT based systems has not been investigated and it is critical that such work is undertaken in the near future if the potential of this novel system is to be achieved.

(7) Although there is clear evidence that the electrostrictive, piezoelectric and energy storage properties of BF-BF are promising for real world applications, there are no studies on pyroelectric and electrocaloric behavior. This oversight in the literature needs redressing.

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