Domain-engineered Lead-Free Relaxor Ferroelectric Ceramics for Enhanced Energy-Storage Performance

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Dielectric capacitors, which store electrical energy in the form of an electrostatic field via dielectric polarization, are used in pulsed power electronics due to their high power density (up to 10^7 W/kg) in comparison with their electrochemical counterparts like electrochemical capacitors ($10\sim10^6$ W/kg) and Li-ion batteries($10\sim100$ W/kg).[1] Despite their desirable power densities, the low energy densities of current dielectric capacitors limit their applications. For example, the energy density of commercial ceramic and polymer dielectrics is less than 2 J cm^{-3}, which is one order of magnitude lower than that of electrochemical capacitors (20 J cm^{-3}). [2] Therefore, dielectric capacitors with a high energy density have been intensively studied over the recent few decades.

The energy density U_e of dielectrics, which is determined by the applied electric field E and the induced dielectric polarization P, can be mathematically expressed by $U_e = \int_{P_r}^{P_m} E\mathrm{d}P$, where P_m and P_r are the maximum polarization and remnant polarization, respectively. Figure 1 shows a unipolar P-E loop of a dielectric, where the blue and red area represent discharged energy density (U_e) and hysteresis loss (U_{loss}) respectively.[3]

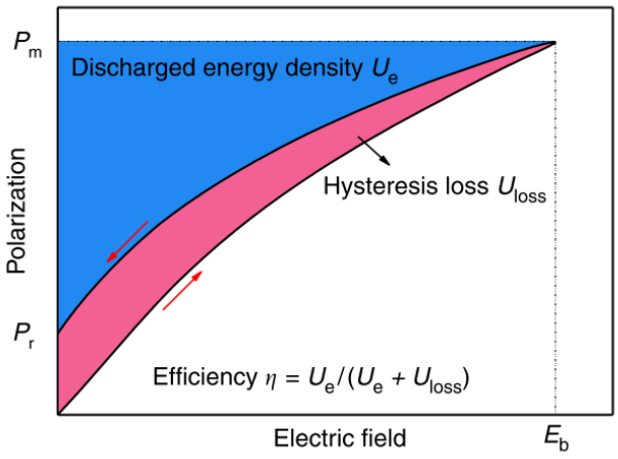

Figure 1. A typical P–E loop of a dielectric and an illustration of (discharged) energy density U_e, hysteresis loss U_{loss}, maximum polarization P_m, remnant polarization P_r, breakdown field E_b and efficiency η. The red arrows indicate the charging and discharging processes.[3]

Ferroelectrics (FEs) and relaxor ferroelectrics (RFEs) are two important classes of dielectric materials. FEs are characterized with high permittivities and strongly nonlinear hysteresis curves with large polarization. However, they demonstrate large hysteresis losses (U_{loss}) with high remnant polarization (P_r) and therefore low recoverable energy density (U_e) and energy efficiency (η). RFEs retain the high permittivities as well as the saturation polarization of normal ferroelectrics but exhibit a significantly lower P_r with slimmer hysteresis loops, which enables them to yield much higher U_e and η (Figure 2). [1,4]

Currently the mainstream RFE materials for energy storage are $PbTiO_3$-based ceramics (spontaneous polarization of $PbTiO_3$ is as high as 86 μC cm^{-2}). Lead-based materials such as $(Pb,La)(Zr,Ti)O_3$, $(Pb,La)(Zr,Sn,Ti)O_3$ and $Pb(Mg,Nb)O_3$–$PbTiO_3$) have been extensively studied as energy storage candidates.[5] However, lead-containing materials pose strong threats to the

environment and human health, which drives the intensive exploration of alternative lead-free materials.[3]

Ferroelectric materials generally consist of small uniform regions with aligned polarization, called "domains". Within each domain, dipoles in each unit cell have the same orientation.[2,6] The optimized properties in RFEs originate from their weakly intercoupled nanodomains that induce lower energy barriers for polarization switching instead of the strongly intercoupled micrometer-size domains in typical FEs.[7] For large-sized ferroelectric domains, a lot of energy will be absorbed by domain aligning and switching in the charge-discharge process and stored as remanence. In contrast, the fast response to the external electric field of small-sized and active polar nanoregions (PNRs) in RFE will result in nearly hysteresis-free polarization responses and high U_e and η (Figure 2). [8,9]

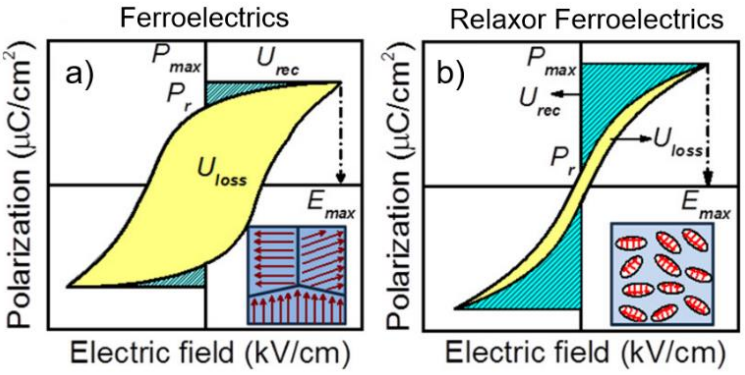

Figure 2. a) Normal ferroelectric behavior with large hysteresis due to its strongly intercoupled micrometer-size domains b) Relaxor-like ferroelectric behavior with slim hysteresis, attributed to the formation of weekly intercoupled polar nano-domains.[4]

Through compositional modulation, such as heterovalent or isovalent ionic substitutions, the long-range ferroelectric order could be broken, and polar nanoregions (PNRs) are generated because of the large local random fields resulting from structural or charge inhomogeneities in a nanoscale. Xuefan et.al. synthesized a series of lead-free relaxor ferroelectric ceramics by incorporating different ratios of $NaTaO_3$ (NT) into $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) by solid state reaction method (reagents are firstly mixed by ball-milling, followed by calcination and sintering), which is denoted as (1-x)BNT-xNT ($0 < x < 1$). [8] The A-site substitution by Na^+ and B-site substitution by Ta^{5+} in perovskite unit cell structure improved the chemical disorder because of the difference in radius and valence state of various cations, which will disrupt the long-range ferroelectric order and lead to highly-dynamic and small-size PNRs. When x=0.20, the ceramics demonstrated both rhombohedral nanodomains and tetragonal polar nanoregions at room temperature, showed slimmer hysteresis with higher η of 85% compared to x=0 (η=4%).

Despite the high energy efficiency, the highest energy density achieved for x=0.2 (4.21 J cm^{-3} at electric field of 38kV/mm) is still not comparable with most lead-based dielectric systems (~20 J cm^{-3})[8]. The low energy density might result from a lower spontaneous polarization of BNT(40 μC cm^{-2})[10] compared to $PbTiO_3$(86 μC cm^{-2}) [2] or a general lower breakdown field for bulk ceramics compared to thin films due to the massive structural defects like pores and impurities.[7] Therefore, RFE thin films with composition of higher spontaneous polarization might achieve better energy storage performance.

$BiFeO_3$ (BFO) is recognized as a potential alternative to lead-based materials, since Bi^{3+} is isoelectronic with Pb^{2+}. In addition, BFO possesses a large spontaneous polarization (~100 μC cm^{-2}). Pan et.al. fabricated a series of solid-solution $(BiFeO_3)_{1-x}$–$(SrTiO_3)_x$ (denoted as BFSTO, $0 < x < 1$) films by pulsed laser depiction(PLD).[3] The author proposed that the incorporating $SiTiO_3$(STO) into BFO (Sr into Bi sites and Ti into Fe sites) induces compositional and chemical disorder in the BFSTO films. An energy storage density of ~70 J cm^{-3} and high energy efficiency of ~70% at electric field of 4.2 MV cm^{-1} were achieved in the BFSTO films. Even though the observed RFE property is favorable for energy storage performance, the BFSTO films demonstrated low maximum polarization P_m(~54 μC cm^{-2} at an electric field of 4.5 MV cm^{-1}) , which indicates there is still much room for further improvement in BFO-based system.

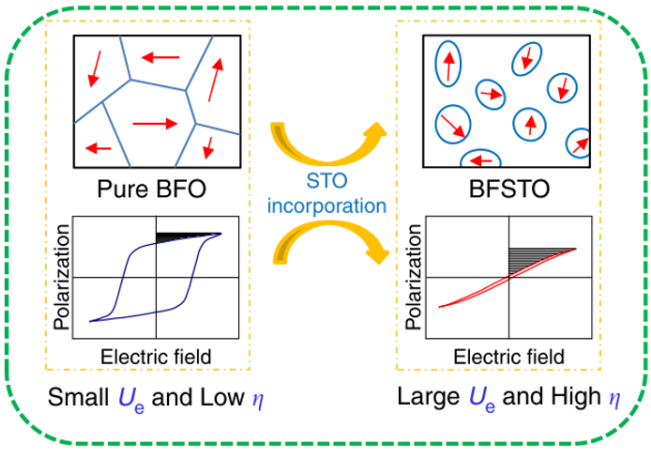

Figure 3. Schematic of domain evolution and FE-to-RFE transition induced by the incorporation of STO into BFO, leading to concurrently improved U_e and η. The blue outlines indicate the ferroelectric domains and the red arrows denote the spontaneous polarization directions.[8]

Since polymorphic nanodomain structure (tetragonal and rhombohedral nanodomains with cubic matrix) has been proposed to exist in BNT-based relaxors[8], Pan et. al. proposed to achieve RFEs with simultaneously high polarization and low loss by introducing polymorphic nanodomains into dielectric films.[7] Guided by phase-field simulations, they fabricated $BiFeO_3$-$BaTiO_3$-$SrTiO_3$(BFO-BTO-STO) ternary solid-solution films, where they combined BFO and BTO to introduce R and T FE phases respectively, and introduced STO to break the long-range FE order and induce nanodomains.(Fig. 3). An energy density of 112 J cm^{-3} with an energy efficiency of ~80% was achieved with minimized hysteresis while maintaining high polarization (69μC cm^{-2} at an electric field of 4.9 MV cm^{-1}). They proposed that the polarization anisotropy and energy barrier between the <111>R and <001>T

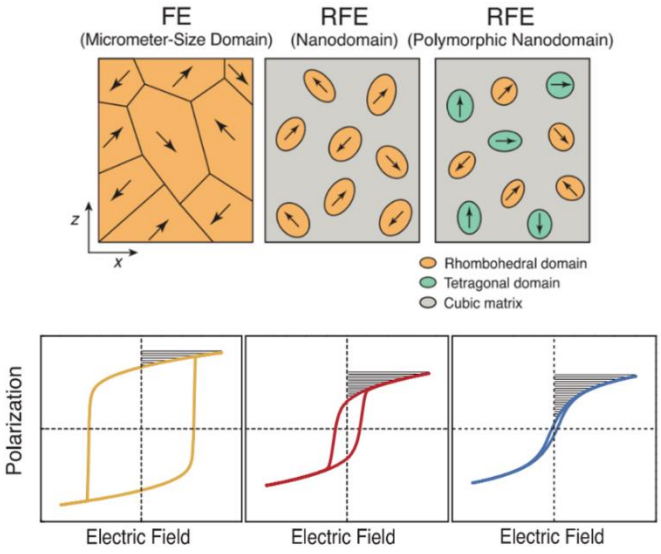

Figure 4. Design of new RFEs with enhanced energy performance via polymorphic nanodomain design. The shadowed area in the P-E loops represents the energy density.[5]

polarization states should be greatly weakened in such polymorphic nanodomain structure. By optimizing the R and T nanodomain compositions, they could minimize both the energy barrier to domain switching and the hysteresis loss while maintaining a high polarization.

This work demonstrates that domain engineering is an important technique for obtaining enhanced energy storage properties in dielectric ceramic materials. The approach of domain engineering through composition design with the aid of phase-field-simulation can be extended to the development of other possible BFO-based RFEs such as BFO-$CaTiO_3$, BFO-$BaZrO_3$, and BFO-$BaSnO_3$ etc. We can also expect to obtain series of new RFE systems with domain engineering by incorporating the above analogous ABO_3 components into other FEs such as $(K,Na)NbO_3$, $LiNbO_3$, and $LiTaO_3$ etc. In addition, other domain engineering methods such as inducing anisotropy and stress in FE films by selected substrate, or poling FE single crystals with selective directions to form a multi-domain configuration[3] have been explored by researchers and provide more possibilities to enhance dielectric capacitor properties.

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