Progress and perspectives in dielectric energy storage ceramics

Dongxu Li\textsuperscript{a,b,†}, Xiaojun ZENG\textsuperscript{a,†}, Zhipeng Li\textsuperscript{a}, Zong-Yang SHEN\textsuperscript{a,*}, Hua HAO\textsuperscript{b}, Wenqin LUO\textsuperscript{a}, Xingcai WANG\textsuperscript{c}, Fusheng SONG\textsuperscript{a}, Zhumei WANG\textsuperscript{a}, Yueming LI\textsuperscript{a}

\textsuperscript{a}Energy Storage and Conversion Ceramic Materials Engineering Laboratory of Jiangxi Province, China National Light Industry Key Laboratory of Functional Ceramic Materials, School of Materials Science and Engineering, Jingdezhen Ceramic University, Jingdezhen 333403, China
\textsuperscript{b}State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China
\textsuperscript{c}Chengdu Hongke Electronic Technology Co., Ltd., Chengdu 610000, China

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Abstract: Dielectric ceramic capacitors, with the advantages of high power density, fast charge-discharge capability, excellent fatigue endurance, and good high temperature stability, have been acknowledged to be promising candidates for solid-state pulse power systems. This review investigates the energy storage performances of linear dielectric, relaxor ferroelectric, and antiferroelectric from the viewpoint of chemical modification, macro/microstructural design, and electrical property optimization. Research progress of ceramic bulks and films for Pb-based and/or Pb-free systems is summarized. Finally, we propose the perspectives on the development of energy storage ceramics for pulse power capacitors in the future.

Keywords: energy storage ceramics; dielectric; relaxor ferroelectric; antiferroelectric; pulse power capacitor

1 Introduction

Electric energy, as secondary energy, plays a dominant role in human daily life, industrial manufacture, and scientific research owing to its cost-effectiveness, versatility, and convenient transportation. Compared with traditional fossil fuels, electrical energy generated from renewable resources can effectively cope with resource depletion and reduce environmental pollution. However, the characteristics of intermittence, fluctuation, and randomness result in a time and space difference between practicality and expected demand, and thereby seriously hinder its large-scale development and application [1]. It is urgent to develop advanced technologies to address the issue of electric energy storage and conversion. Currently, the researches of energy storage technologies are mainly concentrated on dielectric capacitors [2,3], electrochemical capacitors [4], batteries [5], and solid oxide fuel cells [6], whose corresponding characteristics are given in Fig. 1.

Ceramic capacitor, as a passive component, possesses high power density (~GW/kg), fast charge–discharge speed (μs, or even ns), well fatigue endurance (≥ 10\textsuperscript{6} cycles), and high temperature stability, playing an
indispensable role in solid-state power systems [1,7]. Generally, ceramic capacitors with a physical power supply based on dipole orientation, have relatively lower energy density than lithium-ion batteries and solid oxide fuel cells. Therefore, it is critical to improve the energy density of ceramic capacitors for expanding their practical applications.

Polarization behavior of dielectric materials under external electric field can be characterized by $P$–$E$ loops (hysteresis loops) [8,9], as exhibited in Fig. 2. According to different $P$–$E$ loop characteristics, dielectric materials can be classified into linear dielectric, ferroelectric, and antiferroelectric, of which ferroelectric includes normal ferroelectric and relaxor ferroelectric. Based on basic principle and reported literature, the polarization of linear dielectric is linearly proportional to the electric field, whereas its relatively low dielectric constant ($\varepsilon_r$) makes it difficult to achieve high energy density. Normal ferroelectric also possesses limited energy density because of its high remanent polarization ($P_r$). Relaxor ferroelectric and antiferroelectric could achieve both high energy density and efficiency, owing to their relatively high maximum polarization ($P_{\text{max}}$), low remanent polarization ($P_r$), and moderate breakdown strength ($E_b$), and thus have been considered to be the most potential candidates for pulse power systems.

Currently, the researches of energy storage ceramics are mainly concentrated on bulk (> 100 μm), thick film (1–100 μm), and thin film (< 1 μm). It should be noted that these three dielectric ceramics categories possess a big difference in actual energy storage capability, and thus one cannot treat them as one object in the same way. Meanwhile, the device application type also has different categories: ceramic bulk, multilayer structure capacitor, flexible electronic, integrated circuit, etc. This review combines the related work of authors, discusses the progress of energy storage performances of linear dielectric, relaxor ferroelectric, and antiferroelectric with emphasis on composition modification, macro/microstructural modulation, and electrical property optimization.

## 2 Key parameters for evaluating energy storage properties

### 2.1 Energy storage density

Generally, energy storage density is defined as energy in per unit volume ($J/cm^3$), which is calculated by [2]:

$$W = \int_0^{D_{\text{max}}} EdD$$  \hspace{1cm} (1)

where $W$, $E$, $D_{\text{max}}$, and $dD$ are the total energy density, applied electric field, maximum electric displacement at $E$, and increment of electric displacement per unit of the electric field, respectively. For ceramic dielectric, $D$ is an unmeasurable microscopic physical quantity, and is usually expressed by polarization as following:

$$D = \varepsilon_0 E + P$$  \hspace{1cm} (2)

Meanwhile, $P$ is dependent on $E$ as follows:

$$P = \varepsilon_0 \chi E$$  \hspace{1cm} (3)

where $\varepsilon_0$ is the vacuum dielectric constant of $8.854 \times 10^{-12} \text{ F/m}$, $\chi$ is the dielectric polarization coefficient, so
that Eq. (2) can be expressed as

\[ D = \varepsilon_0 (\chi + 1) E = \varepsilon_0 \varepsilon_r (E) E \] (4)

where \( \varepsilon_r (E) \) is the relative dielectric constant at \( E \). Therefore, Eq. (1) after the change is as follows:

\[ W = \int_0^{\Phi_{\text{max}}} \varepsilon_0 \varepsilon_r (E) EdE \] (5)

It is obvious that high \( \varepsilon_r \) and high \( E_b \) are important factors for achieving high \( W \) [10]. However, these two factors are hard to obtain simultaneously in a given material due to the trade-off relationship.

It should be noted that \( W \) is a sum of effective energy density (\( W_{\text{rec}} \)) and energy loss (\( W_{\text{loss}} \)) [8,11]. In practice, \( W_{\text{rec}} \) is more important than \( W \) in evaluating the energy storage performances of dielectric materials. As shown in Fig. 2, \( W_{\text{rec}} \) is determined by the area enclosed by the discharge curve of its \( P-E \) loops and the polarization axis. The equation is given as follows:

\[ W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} E dP \] (6)

Obviously, high \( P_{\text{max}} \), low \( P_r \) (i.e., large \( \Delta P = P_{\text{max}} - P_r \)), and high \( E_b \) are essential factors to achieve high \( W_{\text{rec}} \).

### 2.2 Energy storage efficiency

Energy storage efficiency (\( \eta \)) is another important parameter to evaluate energy storage performances of dielectric materials, which is expressed as

\[ \eta = \frac{W_{\text{rec}} \times 100}{W} = \frac{W_{\text{rec}}}{W_{\text{rec}} + W_{\text{loss}}} \times 100 \] (7)

where \( W_{\text{loss}} \) is the energy loss during the discharge process, which equals to the area enclosed by the \( P-E \) loop in number. \( W_{\text{loss}} \) is mainly dissipated as heat, and a higher value means a stronger negative effect on the service life of ceramic capacitors. Therefore, it is vital that \( P-E \) loops gradually go slim to enhance \( \eta \), and then improve its practical application.

According to Eqs. (6) and (7), \( P-E \) loops go slim accompanied with high \( P_{\text{max}} \), low \( P_r \) (i.e., high \( \Delta P = P_{\text{max}} - P_r \)), and high \( E_b \), which become the key issues in optimizing the energy storage characteristics of dielectric materials. There are two strategies: For one, to optimize the polarization behavior and strengthen their relaxor characteristics, which means that \( P-E \) loops go slim; for the other, to improve the breakdown behavior of dielectric ceramics, i.e., enhancing its \( E_b \).

This paper chooses linear dielectric, relaxor ferroelectric, and antiferroelectric as targets, and discusses the influences of chemical modification and macro/microstructural design on polarization behavior and breakdown strength of dielectric materials.

### 2.3 Rapid charging–discharging characteristics

Generally, energy storage performances of ceramic materials can be reflected by \( P-E \) loops measured by a modified Sawyer–Tower circuit. Meanwhile, the energy storage characteristics of ceramic capacitors, including effective discharging time (\( t_{0.9} \)) and power density (\( P \)), are more accurately reflected by the charging–discharging curve recorded at a specific RLC circuit [12]. The simple equivalent circuit model is exhibited in Fig. 3(a). In the charging process ("1" connected to "3"), the potential difference (\( V \)) between two surfaces of capacitor equals the applied voltage (\( V \)), representing the charging process is finished. And then, the vacuum switches automatically and quickly rotate ("2" connected to "3") to achieve the discharging process. Current flows to the oscilloscope via a load (\( R_0 \)), which is recorded as wave function as a function of time. The discharging density is given by

\[ J(t) = \frac{\int_0^t V(t) I(t) dt}{\varphi} = \frac{\pi V_0^2}{2 \rho R_0} \left( 1 - e^{-\frac{2t}{\tau}} \right) \] (8)

where \( \varphi \) is the effective volume, \( \tau \) is the relaxation time, and \( V(t) \) and \( I(t) \) are the voltage and current as function of time, respectively. Discharging current (\( I \)) and energy density (\( J \)) versus time (\( t \)) are shown in Fig. 3(b).

It is reported that the value of \( J \) calculated by Eq. (8) is generally smaller than that of \( W_{\text{rec}} \). For the reasons, it may be closely related to two factors. Firstly, the domains cannot switch and orientate promptly due to fast discharge speed, and thus the energy is not completely released [13]. Secondly, the circuit has equivalent series resistance that generates Joule energy [14]. In order to acquire higher value of \( J \) and \( W_{\text{rec}} \), reducing domain size (e.g., polar nanoregions) only from material itself may be an effective method [15].

Power density (\( P \)) is also an important parameter of dielectric ceramic capacitors, which is determined as follows:

\[ P = \frac{\pi f \varepsilon_0 \varepsilon_r E_b^2}{2 \tan \delta} \] (9)

where \( f \) is the testing frequency, and the others are the same as those discussed above. It can be seen that high \( \varepsilon_r \), high \( E_b \), and low tan\( \delta \) are the basic requirements of
achieving high $P$. Meanwhile, $P$ has an obvious dependence on frequency ($f$), which means high $f$ corresponds to high $P$. In addition, $t_{0.9}$ is an important factor for influencing the practical application of ceramic capacitors. The smaller the value of $t_{0.9}$, the stronger the pulse current can be generated in a short time. It is worth mentioning that the value of $t_{0.9}$ is dependent on not only the intrinsic properties of the dielectric materials, but also some external factors. For example, Li et al. [15] found that $t_{0.9}$ can be controlled by adjusting the load ($R_0$) in the circuit.

2.4 Reliability of work

No matter with dielectric material or pulse capacitor, the reliability of work is a crucial factor to influence its application scenes. Generally, reliability of work requires keeping stability of electric properties of material and device under thermal, electric, mechanical, magnetic, etc., external field stimulus.

Temperature stability usually requires that dielectric properties and polarization of material have a gentle fluctuation as a function of temperature. For example, dielectric constant needs to maintain a ±15% variation over a temperature range from −55 to 125 °C (X7R), to 150 °C (X8R), and even to 300 °C, especially in high temperature working environments. Therefore, one should know the Joule heat categories: dielectric loss or leakage current, and to solve corresponding issues. Generally, different electric field conditions such as cycle number, frequency, voltage category, magnitude, etc., all require keeping good energy storage stability. Specially, fatigue endurance is a very important issue to influence capacitor working capability. In 2009, Lou [16] reviewed different fatigue mechanisms in ceramic bulks, films, and single crystalline, which help us better understand fatigue behavior of material. In addition, mechanic and magnetic fields both influence its polarization behavior of material, and its importance may be playing a crucial role in the future multifunctional coupling requirement. Therefore, the evaluation criterion of reliability of working should be a complicated project.

3 Dielectric ceramics for energy storage capacitors

As given in Fig. 2, dielectric materials mainly include three categories, namely linear dielectric, relaxor ferroelectric, and antiferroelectric. Therefore, we here compare and analyze the energy storage properties of some representative dielectric ceramic bulks and films.

3.1 Linear dielectric ceramics

Linear dielectric ceramics usually possess characteristics of low $\varepsilon_r$ and $\tan\delta$, as well as moderate $E_b$. It is thereby hard to obtain high $W_{rec}$ despite under high electric field. In this regard, the researches of linear dielectric ceramics are mainly concentrated on increasing $\varepsilon_r$ or improving polarization behavior based on maintaining high $E_b$.

3.1.1 TiO$_2$ based ceramics

TiO$_2$ is a typical linear dielectric, with characteristics of moderate $E_b$ (> 350 kV/cm), low $\tan\delta$ (< 0.1%), dielectric constant (~110), and wide band gap (~3.2 eV), and thus receives wide use in contemporary electronic ceramic industries and photocatalysis field [17–20]. Generally, TiO$_2$ has three crystal structures including orthorhombic brookite, tetragonal rutile, and anatase. The rutile phase is more stable and easier to be synthesized than others, and hence gains more attention in ceramic bulks and films [21,22].

In 2013, Hu et al. [23] firstly reported that (In, Nb)
co-doped TiO2 ceramics displayed a giant dielectric constant (\(> 10^4\)) as well as low tan\(\delta\) (< 5\%), and possessed good temperature and frequency stabilities over a wide temperature range (80–450 K). The authors claim that this phenomenon should be closely related to defect clusters and localized electrons, and thus propose a “localized defect polarization” mechanism. However, the specified reason of giant dielectric constant appearing in donor/acceptor co-doped TiO2 ceramics still has some controversies. Li et al. [24,25] attempted to explain the phenomenon by using an internal barrier layer capacitance (IBLC) model, similar to CaCu3Ti4O12 (CCTO) ceramics from extrinsic factors influencing dielectric constant. Actually, most of subsequent discussion on the physical origin of different-type donor/acceptor co-doped TiO2 ceramics is basically around above two mechanisms [26–28], even though no significant progress has been achieved in \(W_{\text{rec}}\) for donor/acceptor co-doping TiO2 ceramics because of the expense of a rapid reduction in \(E_b\).

In another way, improving the sintering behavior of TiO2-based ceramics would be effectively enhancing \(E_b\), such as refining grain size [17,29], adding glass phase [30], applying special sintering technology (SPS), and so on. Liu et al. obtained a \(W_{\text{rec}}\) of 1.15 J/cm\(^3\) for alkali-free glass modified TiO2 ceramics at 501.7 kV/cm. Unfortunately, \(W_{\text{rec}}\) of those ceramic bulks after different modification ways is still only at a scale of 1 J/cm\(^3\), which is less than other energy storage dielectric materials. It should be noticed that high quality TiO2 film is a good direction owing to their high \(E_b\). For instance, Chao and Dogan [31] fabricated 0.1-mm thick TiO2 films using tape-casting method, which achieve \(W_{\text{rec}}\) of 14 J/cm\(^2\) at 1400 kV/cm.

### 3.1.2 SrTiO3 based ceramics

SrTiO3 (ST) is a cubic paraelectric phase with ABO3 type perovskite structure, accompanying to space group of \(Pm\bar{3}m\) and lattice constant of \(a = 3.905\) Å [32,33]. ST ceramics possess moderate \(\varepsilon_r\) of \(-300\), \(E_b\) of \(-100\) kV/cm, and low tan\(\delta\) of \(-10^{-3}\), as well as good temperature-, frequency-independent dielectric properties, bias voltage stability, and thermoelectric energy conversion efficiency [34–36]. Therefore, it is considered to be a potential energy storage and conversion candidate. Compared with TiO2 ceramic (\(-110\)) and polymer linear dielectric (\(< 10\)), ST has an advantage of relatively high \(\varepsilon_r\), and thus is more suitable for pulse capacitor.

Utilizing Ca\(^{2+}\), Ba\(^{2+}\), and Pb\(^{2+}\) ions to replace Sr\(^{2+}\) on the A-site of ST could adjust the Curie temperature (\(T_C\)) to room temperature, and thus dielectric constant could be enhanced [37,38]. Especially, \(\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3\) (BST) solid solutions combine the characteristics of high \(E_b\) of SrTiO3 and high \(\varepsilon_r\) of BaTiO3, and receive much more attention in recent years [39]. The structure and performance of BST can be adjusted over a wide range to meet the requirements of different applications. As the molar fraction of Ba increases from 0 to 1, phase composition of BST varies from cubic paraelectric (ST) to tetragonal ferroelectric (BT), accompanying by the \(T_C\) increase from near absolute 0 to \(-393\) K. According to theoretical calculation of BST solid solution by Fletcher et al. [40], it is easier to obtain an ideal energy storage property if the \(T_C\) of the ceramic composition is far away the working temperature. Thereby, BST compositions with \(x \leq 0.4\) would be more suitable pulse power capacitor candidates because \(P–E\) loops display linear or weak nonlinear characteristic at room temperature, as shown in Fig. 4. In 2015, Wang et al. [37] investigated energy storage performances of \(\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3\) (\(x \leq 0.4\)) ceramics, and found that \(\text{Ba}_0.4\text{Sr}_{0.6}\text{TiO}_3\) achieved the highest \(W_{\text{rec}}\), while relatively low and rapidly decreased \(\eta\) becomes a serious problem to hinder its application. By comparison, \(\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3\) possessed moderate \(W_{\text{rec}}\), high \(\eta\) (\(\geq 95\%\)), and very low dielectric loss (tan\(\delta\) = 7.6 \times 10^{-4} @ 1 kHz), making it more suitable for the fabrication of solid state compact portable pulse power electronics.

![Fig. 4 Polarization–electric field (\(P–E\)) hysteresis loops of \(\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3\) (BST, \(x \leq 0.4\)) ceramics. The inset shows the effective energy storage and energy loss during the charge–discharge process. Reproduced with permission from Ref. [37], © Elsevier Ltd and Techna Group S.r.l. 2015.](www.springer.com/journal/40145)
For aliovalent doping in A-site of ST, a similar phenomenon with giant dielectric TiO₂ can be observed, and corresponding mechanisms are widely studied. Chen et al. [41–43] reported (Bi,Sr)TiO₃ ceramics with giant dielectric constant, discussed the related physical mechanisms, and proposed that the first and second ionization of oxygen vacancies as well as corresponding thermal movement were the main reasons. To avoid the problem of Bi-containing oxides volatilizing at high temperature, Shen et al. [34,44–46] used trivalent nonvolatile rare earth ions (Re³⁺ = La, Sm, Gd, Er, Nd, etc.) to replace Sr²⁺, and designed three composition formulas based on three possible charge compensation mechanisms such as equimolar substitution, introducing Sr or Ti vacancy in advance, and successfully fabricated ceramics with perovskite structure. It is experimentally verified the feasibility of introducing ion vacancies in advance for charge compensation, and then the concept of “forced charge compensation mechanism” is summarized and proposed. For instance, Shen et al. [44] synthesized Re₀.02Sr₀.97TiO₃ ceramics by introducing Sr vacancy in advance, displaying a high dielectric constant and good bias voltage stability, as shown in Figs. 5 and 6. Furthermore, multiple mechanisms such as Maxwell–Wagner interface polarization, variable charge of Ti element, defect clusters, etc., are all proposed to illustrate donor and/or acceptor doping ST ceramics.

Microstructure regulation plays an important role in enhancing E_b of ST ceramics. In 2014, Song et al. [47] prepared Ba₀.4Sr₀.6TiO₃ ceramics with various grain sizes (0.5–5.6 µm), and observed that dielectric peak gradually depressed and broadened and E_b gradually increased with decreasing grain size, which should be closely related to the ratio of grain/grain boundary and polar nanoregions (PNRs). Ba₀.4Sr₀.6TiO₃ ceramic bulk with grain size of 0.5 µm achieves a high W_rec = 1.28 J/cm³ measured at the highest E_b of 243 kV/cm. Wu et al. [48] compared microstructure and energy storage properties of spark plasma sintered (SPS) and conventionally sintered (CS) Ba₀.3Sr₀.7TiO₃ ceramics. The SPS sintered ceramics consists of tetragonal and cubic phases with an average grain size of 880 nm, while CS ones are only of the tetragonal phase. The maximum W_rec of SPS samples is 1.13 J/cm³ at E_b = 230 kV/cm, which is approximately twice as much as that of CS samples (0.57 J/cm³). In addition, the addition of suitable glass compositions is also an effective method to enhance E_b and reduce the sintering temperature of ST based ceramics [49,50]. In 2019, Shen et al. [51] used a homemade glass frit to modify BST enhancing the E_b and reducing the high temperature resistivity, which expanded the working temperature range for energy storage ceramic capacitor applications.

“Defect engineering” is an effective tool to enhance W_rec by strengthening relaxor characteristics for ST-based ceramic films. Yang et al. [52] fabricated (Sr₁₋₁.₅Biₓ)Ti₀.₉₉Mn₀.₀₁O₃ (SBTM, x = 0.01, 0.05, 0.1) thin films with a thickness of 217 nm using sol–gel method. As x value increases, relaxor behaviors are gradually strengthened due to a slight rotation of the (TiO₆) octahedra induced by the formation of Bi³⁺–V⁰⁰ defect complex. Under an electric field of 1982 kV/cm,
(Sr0.85Bi0.1)Ti0.99Mn0.01O3 possess a $W_{\text{rec}}$ of 24.4 J/cm$^3$ accompanied by the largest $\Delta P$ ($P_{\text{max}}-P_r = 34.3$ µC/cm$^2$). Actually, the introduction of other Bi-contained compounds such as Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) [53], BiFeO$_3$ (BF) [54] has a similar effect to strengthen relaxor characteristics. For example, Pan et al. [54] deposited 5 mol% Mn-doped 0.6SrTiO$_3$–0.4BiFeO$_3$ (0.6ST–0.4BF) thin film on Nb-doped SrTiO$_3$ single crystal substrate using pulsed laser deposition (PLD), and acquired that $W_{\text{rec}}$ and $\eta$ were 51 J/cm$^3$ and 64%, respectively. In addition, the energy storage performances exhibited good temperature stability over (~−40)–140 °C and well fatigue endurance after $2 \times 10^7$ cycles. In the related mechanism studies, Hou et al. [55] investigated the influence of interface difference and thickness on the energy storage performances for ST thin films, and observed the existence of ionic diffusion layers and oxygen vacancies using high resolution transmission electron microscope (HR-TEM). Moreover, they observed that $E_b$ and $P_{\text{max}}$ (up to $10^2$ µC/cm$^2$) along the positive direction were higher than the negative direction. Therefore, a maximum $W_{\text{rec}}$ of ST thin films reach 307 J/cm$^3$ for positive direction, which may be related to local electric field and redistribution of oxygen vacancy.

Various meaningful and interesting works have been done in the optimization of macro/micro structures to improve energy storage properties of ST-based ceramic films. It is well known that the amorphous phase usually possesses higher $E_b$ but lower $\varepsilon_r$ than their crystalline counterparts. Gao et al. [56] studied energy storage behaviors of amorphous ST thin films with different top electrodes, proposed “self-healing” mechanism based on the anodic oxidation reaction in aluminum electrolytic capacitors. At a relative humidity of 60%, amorphous ST films with Al top electrode achieve the $W_{\text{rec}}$ of 15.7 J/cm$^3$ at 3500 kV/cm, which approaches to 8 times of the samples with Au electrode. Since then, Gao et al. [57] inserted insulating Al$_2$O$_3$ as a blocking layer to form heterostructure, and achieved a maximum $W_{\text{rec}}$ of 39.49 J/cm$^3$ at $E_b = 7542.3$ kV/cm when interface number equals 4. Recently, Chen et al. [58] used Ca$_{0.2}$Zr$_{0.8}$O$_{1.8}$ (CSZ) as dead layer to enhance $E_b$ of Ba$_{0.3}$Sr$_{0.7}$Zr$_{0.18}$Ti$_{0.82}$O$_3$ (BSZT) thin films. Due to the formation of a high electron injection barrier, Schottky electron emission is suppressed, and thus $E_b$ and $W_{\text{rec}}$ are enhanced from 5.4 to 6.3 MV/cm and 64.8 to 89.4 J/cm$^3$, respectively. Energy storage properties of partially Pb-free linear dielectric ceramics are summarized and listed in Table 1.

In summary, for linear dielectric ceramic bulks, giant dielectric constant can be observed in TiO$_2$-based with donor/acceptor co-doping at B-site, and ST-based with donor/acceptor co-doping at B-site or aliovalent doping of at A-site bulks by chemical modification. Related physical mechanisms, some controversies, however, are still existed. Energy storage properties of ceramic bulks are limited at expense of a rapid decrease in $E_b$. Adding of suitable glass phase, special sintering technology and refining grain size are both able to enhance $E_b$ of ceramic bulks. For ST-based ceramic films, adjusting suitable ratio of amorphous and crystalline or introducing a high insulating layer would be a good way to improve its breakdown behavior.

### Table 1 Energy storage properties of Pb-free linear dielectric ceramic bulks and films

| Composition          | Category | $t$  | $W_{\text{rec}}$ (J/cm$^3$) | $\eta$ (%) | $\varepsilon_r$ @ RT | $E_b$ (kV/cm) | Ref.    |
|---------------------|----------|------|-----------------------------|------------|----------------------|---------------|--------|
| TiO$_2$ + 15 wt% BBAS | Bulk     | —    | 1.15                        | —          | 103                  | 501.7         | [30]   |
| TiO$_2$             | Thick film | 0.1 mm | 14                          | —          | 108                  | 1400          | [31]   |
| Ba$_{0.1}$Sr$_{0.9}$TiO$_3$ | Bulk     | 0.6 mm | 0.23                        | 95.7       | 650                  | −90           | [37]   |
| Ba$_{0.1}$Sr$_{0.9}$TiO$_3$ | Bulk     | 0.3 mm | 1.28                        | —          | −1500                | 243           | [47]   |
| Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ (SPS) | Bulk     | —    | 1.13                        | 86.8       | —                    | 230           | [48]   |
| (Sr$_{0.85}$Bi$_{0.1}$)Ti$_{0.99}$Mn$_{0.01}$O$_3$ | Thin film | 217 nm | 24.4                        | 64.7       | 550                  | 1380          | [52]   |
| 0.5 mol% Mn-doped 0.6ST–0.4BF | Thin film | 500 nm | 51                          | 64         | 240                  | 3600          | [54]   |
| ST                  | Thin film | 610 nm | 307                         | 89         | −350                 | 6600          | [55]   |
| Amorphous ST        | Thin film | 300 nm | 15.7                        | —          | 29.1                 | −3500         | [56]   |
| ST/4AO              | Thin film | 370 nm | 39.49                       | −15        | 7542.3               | [57]          |
| BSZT                | Thin film | 610 nm | 89.4                        | 65         | −160                 | 6300          | [58]   |

BBAS: BaO–B$_2$O$_3$–SiO$_2$; ST: SrTiO$_3$; BF: BiFeO$_3$; AO: Al$_2$O$_3$; BSZT: Ba$_{0.3}$Sr$_{0.7}$Zr$_{0.18}$Ti$_{0.82}$O$_3$. 

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3.2 Relaxor ferroelectric ceramics

Ferroelectric is a special dielectric material that possesses spontaneous polarization ($P_s$) at a certain temperature range and the direction of $P_s$ can be changed with an external electric field. Compared with linear dielectric, ferroelectric displays an obvious nonlinear characteristic since the domain cannot fast respond to electric field stimulation. Generally, polarization behavior of dielectric material can be characterized by $P-E$ loop, and thus ferroelectric can be classified into normal ferroelectric and relaxor ferroelectric [59], as illustrated in Fig. 7. Normal ferroelectric possesses high $P_{\text{max}}$ while its high $P_t$ leads to that most of energy is dissipated during the discharge process. By contrast, relaxor ferroelectric exhibits slim $P-E$ loop with high $P_{\text{max}}$ and low $P_t$ (i.e., high $\Delta P = P_{\text{max}} - P_t$) meaning that electric energy can be effectively released, and thus obtains better energy storage performances [60]. Note that strengthening the relaxor characteristics and enhancing $E_b$ have become important factors for enhancing $W_{\text{rec}}$. Furthermore, ferroelectric here discussed mainly refers to relaxor ferroelectric.

3.2.1 Pb-based relaxor ferroelectric ceramics

$\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT, $0 \leq x \leq 1$) ceramic located at morphotropic phase boundary (MPB) where Zr:Ti is of 52:48, possesses a high piezoelectric activity ($d_{33}$ up to 300 pC/N) and good temperature stability, and becomes an extremely popular dielectric material [61–63]. In addition, other ceramic compositions such as PZT 65/35, 70/30 also received more attention and no limitation by piezoelectric properties [64,65]. For example, the researches of actuator in PZT ceramics are increasing due to a large electrostrain under low electric field. In 2019, Kumar et al. [66] reported $\text{Pb}_{0.98}\text{La}_{0.011}\text{Zr}_{0.70}\text{Ti}_{0.30}\text{O}_3$ (PLZT 11/70/30) ceramics achieved a $W_{\text{rec}}$ only of 0.85 J/cm$^3$ due to low electric field. Generally speaking, current energy density of Pb-based relaxor ferroelectric ceramic bulks is less than 3 J/cm$^3$. In 2017, Zhang et al. [67] investigated energy storage properties of PbZr$_{0.52}$Ti$_{0.48}$O$_3$-based thin films, acquired a high $W_{\text{rec}} = 28.2$ J/cm$^3$ for PbZrO$_3$/PbZr$_{0.52}$Ti$_{0.48}$O$_3$ bilayer thin films at 2410 kV/cm. In addition, they continued to design a sandwich structure of PbZr$_{0.52}$Ti$_{0.48}$O$_3$/Al$_2$O$_3$/PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PZT/AO/PZT) to enhance $E_b$ [68]. Due to the formation of so-called “built-in electric field” at the interface and the high insulating characteristic of AO, PZT/AO/PZT annealed at 550 °C achieved a $W_{\text{rec}}$ of 63.7 J/cm$^3$ at 5.7 MV/cm. It should be mentioned that PZT 52/48 system still possesses relatively high $P_t$ restricting its energy storage properties.

Generally, a small amount of La$^{3+}$ (about 7–10 mol%) replacing Pb$^{2+}$ would effectively strengthen the relaxor characteristics of PZT-based ceramics owing to a disrupted long-range ferroelectric order and diffuse phase transition [71,72]. $\text{(Pb,La)}\text{(Zr,Ti)}\text{O}_3$ (PLZT) based relaxor ferroelectric is therefore considered to be a promising energy storage ceramic capacitor candidate. Adjusting suitable La/Zr/Ti ratio generates an important influence on electric properties because of the complicated phase structure. For example, Hu et al. [73] investigated the effect of different Zr/Ti ratios on the energy storage properties of PLZT thin films at a fixed La content of 8 mol%. As Ti/(Zr+Ti) ratio gradually increases, $\varepsilon$ enhances while tan $\delta$ shows an opposite trend indicating phase structure gradually transforms from relaxor ferroelectric into normal ferroelectric. At $E_b = 2180$ kV/cm, $W_{\text{rec}}$, $\eta$ of the PLZT 8/52/48 relaxor ferroelectric thin films are 30 J/cm$^3$ and 78%, respectively. In chemical doping, Liu et al. [74] used Mn as a dopant of $\text{(Pb}_{0.9}\text{La}_{0.09})\text{(Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (PLZT 9/65/35) to enlarge the polarization difference of $P_{\text{max}}-P_t$, measured a $W_{\text{rec}}$ of 30.8 J/cm$^3$ for 1 mol% Mn

![Fig. 7 Schematic of hysteresis loop: (a) normal ferroelectric and (b) relaxor ferroelectric.](www.springer.com/journal/40145)
thick films. In addition, the addition of excess Pb is a common chemical compensation method to solve the problems of Pb volatilization during the annealing process, and of suppressing the formation of pyrochlore phase [75].

Reasonable design and selection of heterostructure for Pb-based thin films, is an important step in optimizing energy storage properties. In 2013, Zhang et al. [76] prepared a compositionally gradient (Pb$_{1-x}$La$_x$)(Zr$_{0.65}$Ti$_{0.35}$)O$_3$ (PLZT, $x = 0.08, 0.09, 0.1$) thick films using sol–gel method. Up-graded PLZT films possess a $W_{\text{rec}}$ of 12.4 J/cm$^3$ at 800 kV/cm, down-graded one of 8.9 J/cm$^3$, and the lowest single composition one of 7.1 J/cm$^3$. It is accepted that high texture quality and dense structure are both severely influencing breakdown behaviors and energy storage performances [77,78]. Nguyen et al. [77] deposited (Pb$_{0.9}$La$_{0.1}$)(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PLZT 10/52/48) thick films using PLD on Si substrate choosing Ca$_2$Nb$_3$O$_{10}$ (CNOns) and Ti$_{0.87}$O$_2$ (TiOns) nanosheets as the template layer. Highly textured (001)-oriented PLZT 10/52/48 films grown on CNOns possess a high $W_{\text{rec}}$ of 58.4 J/cm$^3$, which exceeds $W_{\text{rec}}$ of 44 J/cm$^3$ for (110)-oriented PLZT 10/52/48 films grown on TiOns. Generally speaking, there are differences in lattice constants and thermal expansion coefficients in hetero-interfaces, which provide good conditions for stress. Figure 8(a) shows $P$–$E$ loops of PLZT 8/52/48 thick films at different substrates. Ma et al. [69] utilized XRD to analyze residual stress for PLZT 8/52/48 thick films, and considered compressive stress can in a certain extent improve tunability of the polarization, enhance $E_b$ and domain switch ability. In addition, note that Peng et al. [70] recently prepared Mn-doped Pb$_{0.97}$La$_{0.02}$(Zr$_{0.905}$Sn$_{0.015}$Ti$_{0.08}$)O$_3$ (PLZST) relaxor ferroelectric thin films, and innovatively proposed a “low-temperature poling” method to improve $E_b$, and called it “wake-up” mechanism. Figure 8(b) shows $P$–$E$ loops of PLZST films before and after “awaken state”, with the inset showing the $I$–$E$ curve after “awaken state”. Reproduced with permission from Ref. [70], © Elsevier Ltd. 2020.

| Composition | Category | $t$ (μm) | $W_{\text{rec}}$ (J/cm$^3$) | $\eta$ (%) | $\varepsilon_r$ @ RT | $E_b$ (kV/cm) | Ref. |
|-------------|----------|----------|--------------------------|---------|----------------|----------------|------|
| PLZT 11/70/30 | Bulk | 1 mm | 0.85 | 92.9 | −3500 | 85 | [66] |
| PZ/PZT 52/48 | Thin film | 350 nm | 28.2 | −50 | — | 2615 | [67] |
| PZT/AO/PZT | Thin film | 330 nm | 63.7 | 81.3 | −50 | 5711 | [68] |
| PLZT 8/52/48 | Thin film | 690 nm | 30 | 78 | −1500 | 2180 | [73] |
| 1 mol% MnO$_2$ doped PLZT 9/65/35 | Thick film | 1.5 μm | 30.8 | −70 | 1378 | 1679 | [74] |
| Up-graded PLZT | Thick film | 1.5 μm | 12.4 | — | 2170 | 800 | [76] |
| PLZT 10/52/48 | Thick film | 1000 nm | 58.4 | 81.2 | — | 3400 | [77] |
| Low-temperature-poling PLZST | Thin film | 320–350 nm | 31.2 | 60 | — | 2000 | [70] |

PZ/PZT 52/48: Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$; PZT/AO/PZT: Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$/Al$_2$O$_3$/Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$; PLZT 8/52/48: Pb$_{0.97}$La$_{0.02}$(Zr$_{0.905}$Sn$_{0.015}$Ti$_{0.08}$)O$_3$; PLZST: Pb$_{0.97}$La$_{0.02}$(Zr$_{0.905}$Sn$_{0.015}$Ti$_{0.08}$)O$_3$.
3.2.2 Lead-free relaxor ferroelectric ceramics

Lead is a toxic metal, and its volatilization problem at high temperature results in serious environmental and human health concerns. Moreover, some legislation in countries and regions also promote researchers to explore a new lead-free ceramic substitute. Currently, lead-free relaxor ferroelectric ceramics mainly focused on Bi0.5Na0.5TiO3 (BNT), BaTiO3 (BT), BiFeO3 (BF), and K0.5Na0.5NbO3 (KNN) systems, which will be discussed in the following sections.

(1) Bi0.5Na0.5TiO3 based ceramics

Bi0.5Na0.5TiO3 (BNT) is a ferroelectric material firstly discovered by Smolenskii et al. [79], which possesses complicated phase structure and good dielectric, piezoelectric, and ferroelectric properties, especially high $P_{\text{max}}$ (~40 μC/cm²) [80–83]. And so it becomes a popular research topic on fundamental theories and practical studies for ferroelectric materials [84–86]. However, the characteristics of high $P_r$ (~38 μC/cm²), high $E_c$ (~73 kV/cm), and poor sintering behavior for pure BNT ceramics hinder its energy storage applications.

Bi0.5Na0.5TiO3−xBaTiO3 (x = 6%–7%) binary solid solution near MPB exhibits excellent electrical properties, and is a most promising candidate for replacing Pb-based ceramics [87–89]. Since then, extensive energy storage studies have been done on this system. It is particularly important that strengthening dynamic of polar nanoregions (PNRs) through disturbing long-range ferroelectric ordering or expanding nonergodic–ergodic phase transition range both could optimize polarization behavior to obtain high $W_{\text{rec}}$. In 2011, Gao et al. [90] firstly reported that 0.89Bi0.5Na0.5TiO3−0.06BaTiO3−0.05K0.5Na0.5NbO3 (0.89BNT−0.06BT−0.05KNN) ceramics possessed a $W_{\text{rec}}$ of 0.46 J/cm³ at 56 kV/cm. In 2016, Cao et al. [91] used Mn²⁺ to modify 0.7(0.94BNT−0.06BT)–0.3ST ceramics to reduce $P_r$ by forming Mn⁺⁺−V₀ defect complex, which can induce a local electric field influencing domain switch. A $W_{\text{rec}}$ of 1.06 J/cm³ for 1.1 mol% Mn is obtained at 95 kV/cm owing to a large $P_{\text{max}}−P_r$ up to 36.8 μC/cm². Actually, similar phenomenon was already reported by Ren et al. [92]. In 2017, Li et al. [93] incorporated NaNbO₃ into 0.8Bi0.5Na0.5TiO3−0.2SrTiO₃ relaxor ferroelectric ceramics, observed that $P−E$ loop gradually goes slim together with vanished current peaks as NN content increases, which was attributed to the nonergodic–ergodic phase transition. 0.5 mol NaNbO₃ modified ceramics exhibit a high $W_{\text{rec}}$ of 0.74 J/cm³, accompanied by good high temperature energy storage stability and charging–discharging capability. Indeed, delaying the early saturation of polarization is also an effective method to enhance $W_{\text{rec}}$ [94]. In our previous work [37,95], Ba0.3Sr0.7TiO₃, which is suitable for pulse power systems, is selected to improve energy storage performances of BNT-based with an optimized ceramic composition. $P−E$ loop of high $\varepsilon_r$ (Ba₀.₃Sr₀.₇)₀.₃₅(Bi₀.₅Na₀.₅)₀.₆₅TiO₃ (B0.35BNT) relaxor ferroelectric ceramics originally presents an obvious clamped behavior, but its $P_r$ is still high, as shown in Figs. 9(a) and 9(b). We therefore choose

![Fig. 9](a) Temperature dependent dielectric constant and loss of BS,BNT ceramics. The inset is $T_{\text{m}}$ as a function of $x$ value. (b) $P−E$ hysteresis loops of the BS,BNT ceramics with different $x$ value at room temperature. Reproduced with permission from Ref. [95], © The Author(s) 2020.
NaNbO₃ (NN) antiferroelectric to continue to optimize its polarization behavior [96]. 0.94BSBNT–0.06NN relaxor ferroelectric ceramics achieve a high $W_{\text{rec}}$ of 1.25 $\text{J/cm}^3$ at room temperature. Besides, the system exhibits good high temperature stability and fatigue endurance, which may be closely related to the reduction in domain size.

Besides doping modification, multilayer and miniaturization of BNT-based ceramic capacitors are also a significant research direction. In 2018, Li et al. [15] designed a series of $(1-x)$Bi₀.₅Na₀.₅TiO₃–$x$(Sr₀.₇Bi₀.₂)TiO₃ (NBT–xSBT, $x = 0.3–0.5$) ceramics, and corresponding multilayer ceramic capacitors (MLCC) with a single layer thickness of 20 μm were fabricated. A high $W_{\text{rec}}$ of 9.5 $\text{J/cm}^3$, together with $\eta$ of 92%, is achieved in NBT–0.45SBT MLCC. Furthermore, energy storage properties of MLCC display good temperature stability, fatigue endurance, and charging–discharging capability. Recently, Li et al. [97] attempted to enhance $E_r$ through controlling grain orientation, and investigated energy storage performances of NBT–0.35SBT MLCC under different stress states. By comparison, Yang et al. [98] reported energy storage properties of gradient structure (SrTiO₃ + 0.5 wt% Li₂CO₃)/(0.93Bi₀.₅Na₀.₅TiO₃–0.07Ba₀.₉₄La₀.₀₄Zr₀.₀₂Ti₀.₉₈O₃) (STL/(BNT–BLZT)) ceramics along thickness direction. A high $W_{\text{rec}}$ of 2.72 $\text{J/cm}^3$ for STL/(BNT–BLZT) ceramics is obtained at 294 kV/cm. Due to the strict requirements of the harsh working environment such as high temperature (> 200 °C), good insulation and antioxidant, MLCC would encounter many challenges in the future [99,100]. Meanwhile, material system selection, electrode design such as equivalent series resistance (ESR) and loss, cost control of fabrication, and so on, need further consideration.

The volatilization of Bi and Na and variable valence of Ti are easy to generate oxygen vacancy for BNT-based thin films resulting in a large leakage current. Single mental oxides (MnO₂ [101,102], Fe₂O₃ [103], etc.) are used to modify BNT films, which would form different defect complexes to compensate charge balance and suppress oxygen vacancy migration. For example, Mn-doped BNT thick films display a reduced leakage current due to the formation of Mn⁺⁺–V₆⁻ defect complex, which gives rise to a $W_{\text{rec}}$ of 30.2 $\text{J/cm}^3$ for $x = 0.01$ composition [102]. In addition, controlling annealing temperature also has a similar effect on reducing leakage current [104]. In addition, Peng et al. [105] deposited La/Zr modified 0.94BNT–0.06BT high epitaxial quality thin films using PLD, and $P_{\text{max}}$ can reach to 10² $\mu\text{C/cm}^2$ scale due to the complicated phase composition and great relaxor dispersion. (100) and (111) oriented (Bi₁₂/Na₁/2)₀.₉₁₈La₀.₀₂Ba₀.₀₅Z₂(Ti₀.₉₇Zr₀.₀₃)O₃ (BNLBTZ) thin films achieve maximum $W_{\text{rec}}$ of 137 and 154 J/cm³, respectively, far exceeding other Pb-free even Pb-based systems.

Distinguished from single composition of MLCC, macrostructure modification of BNT-based films mainly focuses on gradient composition. It is widely accepted that BNT-based ceramic film is p-type conductivity due to many vacancies generating acceptor states in the band gap, and thus p–n junctions and block layers are applied to inhibit charge transportation. For instance, Guo et al. [106] reported the introduction of Bi₁₀.₅La₀.₇₅TiO₂ (BLT) and Pb(Zr₀.₄Ti₀.₆)O₃ (PZT) dielectric layer on pyroelectric and ferroelectric properties of 0.94BNT–0.06BT ceramic films, and observed leakage current reduce about 3 orders of magnitude. Besides, Chen et al. [106] studied the effect of interface number on energy storage properties of 0.94{(Bi₀.₅Na₀.₅)TiO₃–0.06BaTiO₃/BiFeO₃ (abbreviated as BNBT/nBFO) multilayer film capacitors under a given total thickness, BNBT/2BF thin films exhibit a $W_{\text{rec}}$ of 31.96 $\text{J/cm}^3$ and a $\eta$ of 61% at 2400 kV/cm owing to enhanced insulating characteristic and high polarization. With the rapid development of flexible wearable materials in recent years, related researches on their energy storage performances have gradually increased. Qian et al. [107] prepared a multilayer (Na₀.₅K₀.₅)₆.₅Bi₅.₅TiO₁₅/0.6(Na₀.₅K₀.₅)₆.₅Bi₅.₅TiO₁₅–0.₄8SrTiO₃ (NKBT/NKBT–ST)$_N$ ($N = 2, 3, 6, 8$) films on the F-Mica substrate, with measured $W_{\text{rec}}$ of 73.7 $\text{J/cm}^3$ at 3077 kV/cm for $N = 6$. Under different conditions such as (–50)–200 °C, 10⁸ cycle numbers, 10⁴ bending tests, energy storage performances of (NKBT/NKBT–ST)$_6$ ceramic films both maintain good stability. Energy storage performances of BNT-based relaxor ferroelectric materials are summarized and listed in Table 3.

(2) BaTiO₃-based ceramics

BaTiO₃ (BT) with simple perovskite structure possesses moderate Curie temperature ($T_C$) of 120 °C and corresponding high $\epsilon_r$ of 10⁴ [109,110], and becomes a common dielectric material in passive capacitor. BT-based materials also received more attention in memory and memristor for information processing.
storage and transfer. In addition, the structure and physical property research of BT-based materials still attract more attentions [111–113]. However, pure BT ceramic has some problems such as high P, the reduction from Ti$^{4+}$ to Ti$^{3+}$ at high temperature, which restrict it to achieve high $W_{\text{rec}}$ [114].

In 2009, Ogihara et al. [115] synthesized a temperature stable 0.7BaTiO$_3$–0.3BiScO$_3$ (0.7BT–0.3BS) relaxor ferroelectric ceramics with a thickness of 0.2 mm, and obtained $W_{\text{rec}}$ of 2.3 J/cm$^3$ at 225 kV/cm. When thickness reduces to 15 μm, $W_{\text{rec}}$ enhances to 6.1 J/cm$^3$ at 730 kV/cm. By comparison, Wu et al. [116] utilized BiScO$_3$ (BS) as shell material to coat BT, and $W_{\text{rec}}$ only of 0.68 J/cm$^3$ was measured at $E_b = 120$ kV/cm for BT@3 mol% BS ceramics. Yuan et al. [117] prepared Bi(Mg$_{1/2}$Zr$_{1/2}$)$_2$O$_3$ (BMZ) modified BT-based relaxor ferroelectric, and achieved a high $W_{\text{rec}} = 2.9$ J/cm$^3$ for 0.85BT–0.15BMZ ceramics higher than pure BT ceramics (0.4 J/cm$^3$), and corresponding $P$–$E$ loop is illustrated in Fig. 10(a). The authors thought the enhancement of $W_{\text{rec}}$ is related to PNRs, as evidenced by piezoelectric force microscope (PFM) and transmission electron microscope (TEM). It should be mentioned that other systems such as BaTiO$_3$–Bi(Mg,Ti)O$_3$ (BT–BMT) also display good energy storage capabilities due to the low tolerance factor of ceramic has some problems such as high $P$, which gets a good balance, BCZT-based ceramics would be a promising energy storage candidate.

“Core–shell” structure is a common way of modifying BT-based ceramics, especially in enhancing temperature stability for ceramic capacitor applications. In 2014, Su et al. [124] coated BT nanocrystals with 65PbO–20B$_2$O$_3$–15SiO$_2$ and 65Bi$_2$O$_3$–20B$_2$O$_3$–15SiO$_2$ glass phases, reducing sintering temperature to 900 °C. Meanwhile, the authors estimated $W_{\text{rec}}$ approaching to 10 J/cm$^3$ by equation for Bi-based glass phase. Similarly, high $E_b$ materials such as SiO$_2$ [125] and SrTiO$_3$ (ST) [126] are both used as shell materials to improve breakdown behavior. For example, Wu et al. [126] fabricated BT@ST relaxor ferroelectric ceramics using the sol-precipitation approach, and EDS analysis illustrated BT@ST ceramics in Fig. 10(b). However, with a $W_{\text{rec}}$ only of 0.22 J/cm$^3$ at 47 kV/cm, $\eta$ approaches to 90%. It should be pointed that high $E_b$ materials usually possess low $\varepsilon_r$, and so $W_{\text{rec}}$ of coated BT ceramics cannot be effectively enhanced at the sacrifice of $\varepsilon_r$. Bi-based materials such as BiScO$_3$ as shell material also suffer from the same problem of obtaining high $W_{\text{rec}}$. The reason needs to be further explored due to the complex composition gradient.

Table 3 Energy storage characteristics of BNT-based relaxor ferroelectric ceramic bulks and films

| Composition | Category | $t$ (μm) | $W_{\text{rec}}$ (J/cm$^3$) | $\eta$ (%) | $E_b$ (kV/cm) | Ref. |
|-------------|----------|---------|-----------------|---------|---------|-----|
| 0.89BNT–0.06BT–0.05KNN | Bulk | 0.5 | 0.46 | — | — | 2000 | 56 | [90] |
| 1.1 mol% Mn doped 0.7(0.94NBT–0.06BT)–0.3ST | Bulk | — | 1.06 | — | — | 95 | [91] |
| 0.95(0.85BT–0.2ST)–0.05NN | Bulk | — | 0.97 | 55 | — | 70 | [93] |
| 0.94Bi$^{0.3}$BNT–0.06NN | Bulk | 0.3–0.35 mm | 1.25 | 76 | — | 3800 | 116 | [96] |
| 0.55BNT–0.45ST | Bulk | 20 μm @ SL | 9.5 | 92 | — | 2500 | 72 | [15] |
| STL/(BNT–BLZT) | Bulk | 0.2 mm | 2.72 | 74 | — | 900 | 294 | [98] |
| 0.01 mol Mn doped BNT | Thick film | 1200 nm | 30.2 | 47.7 | — | 400 | 2310 | [102] |
| (111)-oriented BNLBTZ | Thin film | 350 nm | 154 | 95 | — | 2000 | 3500 | [105] |
| 0.94BNT–0.06BT/2BF | Thin film | 400 nm | 31.96 | 61.61 | — | 500 | 2400 | [106] |
| (NKBT/NKBT–ST)_{1–s} | Thin film | 260 nm | 73.7 | 68.1 | — | 600 | 3072 | [107] |

BNT: Bi$^{0.5}$Na$^{0.5}$TiO$_3$; BT: BaTiO$_3$; KNN: K$^{0.5}$Na$^{0.5}$NbO$_3$; ST: SrTiO$_3$; NN: NaNbO$_3$; BS: BiScO$_3$; BNT: (Ba$_{0.7}$Sr$_{0.3}$)$_{0.35}$(Bi$_{0.5}$Na$_{0.5}$)$_{0.65}$TiO$_3$; ST: Sr$_{0.7}$Bi$_{0.2}$TiO$_3$; BLZT: (Bi$_{0.91}$La$_{0.02}$)(Ti$_{0.97}$Zr$_{0.03}$)O$_3$; BS: Bi$^{0.5}$Mg$^{0.5}$Zr$_{0.25}$O$_3$ (BMZ); KNN–ST: (Na$_{1–s}$K$_{s}$)$_{0.5}$Bi$_{0.5}$TiO$_3$; STL: SrTiO$_3$+0.5 wt% Li$_2$CO$_3$; BNT–BLZT: (Bi$_{0.93}$Na$_{0.07}$)(Ti$_{0.98}$Zr$_{0.02}$)O$_3$; BNLBTZ: (Bi$_{0.91}$La$_{0.02}$)(Ti$_{0.97}$Zr$_{0.03}$)O$_3$; BF: BiFeO$_3$; NKBT: (Na$_{0.8}$K$_{0.2}$)$_{0.5}$Bi$_{0.5}$TiO$_3$. SL means single layer.
storage performances of BZT-based ceramic systems receive more attention. Instan et al. [130] prepared 400 nm <100>-oriented Ba(Zr_xTi_{1-x})O_3 (x = 0.3, 0.4, 0.5) relaxor ferroelectric thin films using PLD on La_{0.5}Sr_{0.5}MnO_3/MgO substrates. Importantly, W_{rec} of all ceramics can reach a scale of 10^2 around E_b \approx 3 MV/cm, and a maximum W_{rec} of 156 J/cm^3 is obtained at x = 0.3 composition. In 2017, Cheng et al. [127] reported the influence of thickness and substrate categories on domain/phase of Ba(Zr_{0.2}Ti_{0.8})O_3 thin films. With increasing thickness, mismatch stress gradually releases and rhombohedral phase content increases, as well as twined domain structure is formed, as shown in Fig. 10(c). A high W_{rec} of 166 J/cm^3 for Ba(Zr_{0.2}Ti_{0.8})O_3 thin films is achieved at E_b \approx 5.7 MV/cm. In addition, oxygen pressure is found to generate a positive effect on energy storage properties of BT-based thin films [131].

“Interface engineering”, including interface compatibility, periodic number, and space charge, plays a critical role in enhancing E_b and optimizing polarization behavior of BT-based ceramic films. In 2012, Ortega et al. [132] deposited BaTiO_3/Ba_{0.3}Sr_{0.7}TiO_3 superlattice thin films on MgO single substrate using PLD, and acquired a W_{rec} of 12.24 J/cm^3 measured by P–E loop. It should be noted that a theoretical value of W_{rec} = 46 J/cm^3 at E_b reach to 5.8–6 MV/cm. Sun et al. [133] studied energy storage properties of laminated Ba_{0.7}Ca_{0.3}TiO_3/BaZr_{0.2}Ti_{0.8}O_3 (BCT/BZT) thin films with two layers as a period and the number is 2, 4, 8. With increasing period, E_b enhances from 3 to 4.5 MV/cm, and a maximum W_{rec} is 52.4 J/cm^3 for N = 8. Meanwhile, a series of multilayer structures consisting of two materials or a stack of different dielectric layers, have become the most charming model systems since some unique properties can be enhanced. Due to the difference of electric properties in stacked dielectric material, some physical mechanisms such as current leakage mechanism and charge distribution in heterostructure interface, still need to be further investigated [134,135]. Energy storage performances of the BT based relaxor ferroelectric materials are summarized and listed in Table 4.

(3) BiFeO_3-based ceramics

BiFeO_3 (BF) as a multiferroic material with perovskite structure exhibits high T_C (~850 °C), high P_s (~100 μC/cm^2), and large S_{max} (~0.4 %), and gains extensive studies in different cross fields such as piezoelectric, magnetic, and quantum [136–139]. The volatile nature of Bi and multiple valence variation of Fe during sintering cause large dielectric loss and leakage current [140]. Nevertheless, BF relaxor ferroelectric is
Table 4  Energy storage properties of BT-based relaxor ferroelectric ceramic bulks and films

| Composition | Category | t   | Wrec (J/cm³) | η (%) | εr @ RT | Eb (kV/cm) | Ref. |
|-------------|----------|-----|-------------|-------|---------|------------|-----|
| 0.7BT–0.3BS| Bulk     | 0.2 mm | 2.3 | — | —900 | 225 | [115] |
| BT@3BS      | Thick film | 15 μm | 6.1 | — | 750–800 | 730 | [116] |
| 0.85BT–0.15BMZ | Bulk | — | 6.8 | 81 | —1500 | 120 | [117] |
| BT with BBS glass | Bulk | — | —10 | — | —550 | —1140 | [124] |
| BT@ST       | Bulk     | — | 0.22 | —90 | —2000 | 47 | [126] |
| <100>-oriented Ba(Zr0.3Ti0.7)O3 | Thin film | 400 nm | 156±1 | 72.8 | —3400 | 3000 | [130] |
| Ba(Zr0.2Ti0.8)O3 | Thin film | 350 nm | 166 | —90 | —350 | 5700 | [127] |
| Superlattice BT/BST | Thin film | 0.6 μm | 6.12 | —12.24 | —800 | 1660 | [132] |
| (BCT/BZT)3–4 | Thin film | 100 nm | 52.4 | 72.3 | —175 | 4700 | [133] |

BT: BaTiO3; BS: BiScO3; BMZ: Bi(Mg1/2Zr1/2)O3; BBS: 65Bi2O3–20B2O3–15SiO2; ST: SrTiO3; BST: Ba0.3Sr0.7TiO3; BCT: Ba0.7Ca0.3TiO3; BZT: BaZr0.2Ti0.8O3.

still considered as a potential candidate for energy storage capacitors because of high Ps.

BiFeO3-xBaTiO3 (BF–xBT, 0 ≤ x ≤ 0.5) ceramics maintain high Tc, good ferroelectric and piezoelectric properties resulted from complicated phase structure evolution. With increasing x value, BF–xBT ceramics possess a high Pmax near MPB of BT ≈ 0.33 mol [141–143]. Energy storage properties of BF-based ceramics, therefore, basically are around BF–0.33BT system to reduce Pr. For example, Liu et al. [144] added Ba(Zn1/3Ta2/3)O3 (BZT) into BT–0.34BT relaxor ferroelectric ceramics obtaining a Wrec of 2.56 J/cm³ at 160 kV/cm. To enhance breakdown strength of BF-based ceramics, Qi et al. [145] introduced NaNbO3 (NN) combined with 0.1 wt% MnO2 and 2 wt% BaCu(B2O5) (BCB) as sintering aids to modify 0.67BF–0.33BT relaxor ferroelectric ceramics, and corresponding Weibull distribution of Eb is given in Fig. 11(a). At 360 kV/cm, x = 0.1 sample possesses a maximum Wrec of 8.12 J/cm³ accompanied to η of 90%, which is related to the existence of nanodomain and high density. In addition, Wang et al. [146] reported that Wrec of 0.62BF–0.3BT–0.08Nd(Zr0.5Zn0.5)O3 ceramic bulks is 2.45 J/cm³ at 240 kV/cm. When an MLCC device based on this system is made, Wrec is enhanced to 10.5 J/cm³.

Similar to BF–xBT systems, ST modified BF-based energy storage ceramics are mainly concentrated on films due to thickness limitation. In 2013, Correia et al. [147] prepared 0.4BF–0.6ST thin films using PLD, obtained a high Wrec of 18.6 J/cm³ at 972 kV/cm. Recently, Pan et al. [148] reported (0.55–x)BF–xBT–0.45ST (x = 0–0.4) thin films with polymorphic nanodomain structure are grown on Nb-doped SrTiO3 single crystal substrate. Under an electric field of 4.9 MV/cm, x = 0.3 composition achieves a maximum

![Fig. 11](https://example.com/f11.png)

**Fig. 11**  (a) Weibull distribution and calculated Eb values of (0.67–x)BF–0.33BT–xNN ceramics. Reproduced with permission from Ref. [145], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019. (b) P–E loops from two film capacitor structures before and after the introduction of an alumina layer at the electrode–0.6BF–0.4ST interface. Reproduced with permission from Ref. [150], © AIP Publishing 2012.
due to MPB located at KNbO3 content of 47.5% [154].

KNN materials concentrate on piezoelectric properties since the 1950s at latest century, the researches of with high of "soft layer" with high polarization and "hard layer" possesses a moderate 420 KNbO3 ferroelectric and NaNbO3 antiferroelectric, and insulating layer enhances energy storage performances of the by sol–gel methods, and achieved a high P–E loops, before and after inserting Al2O3 layer were illustrated in Fig. 11(b). Interface polarization behavior to some degree increases hysteresis loss while Al2O3 insulating layer enhances $E_b$, and thus $W_{rec}$ enhances from 13 to 17 J/cm$^3$. Since then, a sandwich structure of "soft layer" with high polarization and "hard layer" with high $E_b$ are constructed to prevent "electric tree" growth and achieve high $W_{rec}$ [151]. It is particularly important that strong interface coupling factors should be considered in designing structure and analyzing properties [152]. Energy storage performances of the BF-based relaxor ferroelectric materials are summarized and listed in Table 5.

(4) $K_0.5Na_{0.5}NbO_3$-based ceramics

$K_0.5Na_{0.5}NbO_3$ (KNN) is a binary solid solution of KNbO3 ferroelectric and NaNbO3 antiferroelectric, and possesses a moderate $d_{33}$ around 80 pC/N, high $T_c$ of 420 °C, and complicated phase structure [153,154]. Since the 1950s at latest century, the researches of KNN materials concentrate on piezoelectric properties due to MPB located at KNbO3 content of 47.5% [154]. The ratio of K/Na has a slight variation while mainly concentrated on 0.5/0.5. However, narrow sintering temperature range, easy volatilization characteristic of K, Na at high temperature both hinder its applications.

In 2016, Du et al. studied KNN-based energy storage ceramics, and achieved a high $W_{rec}$ of about 4 J/cm$^3$ for SrTiO3 (ST) [155] and Bi(Mn$_{0.005}$Nb$_{0.995}$)O$_3$ (BMN) [156] modified KNN ceramics. And they further used CuO [157], ZnO [158], etc., as fruit to improve sintering behavior of KNN-based ceramics. It should be noted that modified KNN-based energy storage ceramics with superfine grain size possess not only high $E_b$ but also good transparency. In addition, utilize “phase boundary engineering” of KNN ceramics to enhance electric properties is a useful method. Recently, Yang et al. [159] proposed “morphotropic relaxor boundary (MRB)” in BT modified KNN ceramics to illustrate an obvious enhancement of electrostrain and dielectric permittivity. At the MRB the electrostrain increases by ~3 times and the permittivity increases by ~1.5 times over a wide temperature range of more than 100 K, as compared with off-MRB compositions. In comparison, the studies of KNN-based ceramic films for energy storage are relatively less, which should be related to insolubility of Nb and volatilization of K and Na. In 2017, Won et al. [160] reported 6 mol% BiFeO3-doped ($K_{0.5}Na_{0.5})(Mn_{0.005}Nd_{0.95})O_3$ (KNMN) thick film possessed a slim P–E loop, and achieved a $W_{rec}$ of 20 J/cm$^3$, $\eta$ of 90.3%. Recently, Huang et al. [161] also used MnO$_2$ to reduce leakage current of 0.95($K_{0.6}Na_{0.4}Li_{0.1})Nb_{0.8}Ta_{0.2})O_3$–0.05CaZrO$_3$–x mol% Mn (KNN–LT–CZ5–x mol% Mn) thin films prepared by sol–gel methods, and achieved a high $W_{rec} = 64.6 J/cm^3$ under an electric field of 3080 kV/cm at $x = 0.5$ composition. Energy storage properties of KNN-based relaxor ferroelectric ceramics and films are summarized and listed in Table 6.

In summary, for relaxor ferroelectric ceramics, the formation of PNRs due to disturbed long-range ferroelectric order or nonergodic–ergodic phase transition can strengthen relaxor characteristics. Reflecting on macroscopic ferroelectric properties, $P–E$ loop goes

| Composition | Category | $t$ (mm) | $W_{rec}$ (J/cm$^3$) | $\eta$ (%) | $\epsilon_r$ @ RT | $E_b$ (kV/cm) | Ref. |
|-------------|----------|----------|----------------------|-----------|------------------|--------------|-----|
| 0.6BF–0.34BT–0.06BZT | Bulk | 0.2 | 2.56 | 70 | — | 160 | [144] |
| 0.57BF–0.33BT–0.11NN | Bulk | 0.15 | 8.12 | 90 | — | 360 | [145] |
| 0.62BF–0.3BT–0.08NZZ | Bulk | 16 μm @ SL | 10.5 | 87 | — | 700 | [146] |
| 0.4BF–0.6ST | Thin film | 400 nm | 18.6 | >85 | — | 972 | [147] |
| 0.25BF–0.3BT–0.4ST | Thin film | 450–500 nm | 112 | 80 | — | 4900 | [148] |
| Dead layer engineered 0.6BF–0.4ST | Thin film | 400 nm | 17 | — | — | — | [150] |

BF: BiFeO3; BT: BaTiO3; BZT: Ba(Zn$_{0.5}$Ta$_{0.5}$)O$_3$; NN: NaNbO3; NZZ: Nd(Zn$_{0.5}$Zr$_{0.5}$)O$_3$; ST: SrTiO3. SL means single layer.
performances. are all important factors to influence energy storage etc., gradient sequence, template or new inert layers such as lattice constant, thermal expansion coefficient, of ceramic films, match degree of physical paraments optimize polarization behavior. In the heterostructure other one, strengthen its relaxor characteristics and of vacancy defect to reduce leakage current; for the other roles: For one, suppress the generation and transportation of vacancy defect to reduce leakage current; for the other one, strengthen its relaxor characteristics and optimize polarization behavior. In the heterostructure of ceramic films, match degree of physical paraments such as lattice constant, thermal expansion coefficient, etc., gradient sequence, template or new inert layers are all important factors to influence energy storage performances.

3.3 Antiferroelectric ceramics

As a special group of ferroelectric material, antiferroelectric has many similarities with ferroelectric whereas still exists obvious differences. In 1951, Kittel [162] originally proposed the concept of antiferroelectric, predicted the existence, and gave some basic characteristics. Generally speaking, antiferroelectric materials possess $P_t$ in a unit cell, but the direction of $P_t$ is antiparallel to that of neighboring unit cell. Antiferroelectric, therefore, does not exhibit polarization in macroscopic characteristics. It is particularly important that antiferroelectric exists a unique feature: double hysteresis loop under an external field. $P$ is linearly proportional to $E$ at a low electric field. When $E$ exceeds the forward switching (AFE-to-FE) field $E_{A-F}$, antiferroelectric displays an obvious ferroelectric behavior, and $P$ fastly increases and gradually reaches $P_{\text{max}}$. Note that antiferroelectric can undergo a ferroelectric–antiferroelectric phase transition field ($E_{F-A}$) after removing $E$. Consequently, $P$ gradually reduces and returns to the initial state (that is, $E = 0$, $P_t = 0$). A similar variation in $P$ can be observed as $E$ continuously increases in an opposite direction.

It is hard to see a double hysteresis loop for most pure antiferroelectric materials at a low electric field, which usually requires special conditions of high temperature and strong electric field to stimulate. Thereby, it is a crucial challenge for antiferroelectric to obtain double $P-E$ loop especially for ceramic bulks. In addition, a typical high squareness $P-E$ loop, and corresponding internal strain induced by antiferroelectric–ferroelectric phase transition both result in low $W_{\text{rec}}$ and reduced device life [12]. In this regard, how to stabilize and relax the antiferroelectric phase (corresponding to enhancing $E_{A-F}$, reducing the difference of $E_{A-F-E_{F-A}}$) and enhance $E_h$ has become a particularly important issue to acquire good energy storage performances.

3.3.1 Pb-based antiferroelectric ceramics

(1) PbZrO$_3$

PbZrO$_3$ (PZ) is the prototype antiferroelectric, and serves as a model system to be thoroughly studied so far. The origin of the phase transition mechanism, however, is not well understood [163]. Despite this, a characteristic double $P-E$ loop with high $P_{\text{max}}$ and low $P_t$ makes it suitable for energy storage capacitors. PZ-based energy storage ceramics gain increasing attention since Chen et al. [164] reported $W_{\text{rec}}$ of 7.1 J/cm$^3$ for PZ thin films during phase transition, but basically around ceramic films.

It is widely accepted that tolerance factor $t$ of perovskite structure is closely related to phase stability, and the equation is represented as

$$t = \frac{r_A + r_O}{\sqrt{2} (r_B + r_O)} \quad (10)$$

where $r_A$, $r_B$, $r_O$ denote ion radius of A, B, and O, respectively. In general, AFE phase can be stabilized for $t < 1$, and reducing $t$ can enhance in some degree the stability of AFE phase. For example, Hao et al. [165] substituted Pb$^{2+}$ (1.20 Å) with smaller Sr$^{2+}$ (1.12 Å) to reduce $t$, and $P-E$ loop goes slim together with increased $E_{A-F}$ and decreased $\Delta E$. As a consequence, (Pb$_{0.95}$Sr$_{0.05}$)ZrO$_3$ (PSZ5) thin films obtain a $W_{\text{rec}}$ of
Choosing smaller ion radius while aliovalent of La$^{3+}$ as donor dopant has a similar effect [166]. In addition, controlling the orientation of PZ thin film also achieves the purpose of stabilizing the antiferroelectric phase. PZ thin film with (100) orientation needs a higher electric field than with (111) one to finish antiferroelectric–ferroelectric phase transition [167].

Tailoring local electric field and stress to enhance $W_{rec}$ is hard but interesting work. As is well known, introducing a new nanoparticle in materials often brings novel properties and improved properties. For example, Sa et al. [169] used α-Fe$_2$O$_3$ nanoparticles to modify PZ thin films, obtained a $W_{rec}$ of 17.4 J/cm$^3$ and $P_{max}$ as high as 78 μC/cm$^2$, attributing to the local field effect. By comparison, Chen et al. [170] fabricated a self-assembled PZ: NiO nano-columnar composite using PLD, and proposed that tensile stress mainly comes from the interface of two phases. At $E_b = \approx 1000$ kV/cm, 5 vol% NiO thin films possess a high $P_{max}$ of $\approx 91$ μC/cm$^2$, and $W_{rec}$ of 24.6 J/cm$^3$. Meanwhile, Ge et al. [171,172] also did a series of works on optimizing polarization behavior mainly such as enhancing $P_{max}$, reducing $\Delta E_{A–F–E}$ using the stress engineering method. To our best knowledge, it is difficult to directly measure and characterize local electric field and stress, and thus corresponding methods need to be developed. Furthermore, the gradient sequence of thin film is significant for enhancing $W_{rec}$. Ye et al. [168] reported a $W_{rec}$ of 16.3 J/cm$^3$ for down-graded higher than that of 9.7 J/cm$^3$ for up-graded PZ-based thin films, and corresponding $P–E$ loops are shown in Fig. 12.

It should be mentioned that PbHfO$_3$ (PHO) antiferroelectric ceramics have some similarity with PZO, and thus the related studies still concentrate on phase structure [173–175]. Nevertheless, the energy storage properties of PHO-based ceramics have rarely been reported. In 2020, Chao et al. [176] prepared Pb$_{0.98}$La$_{0.02}$(Hf$_{0.58}$Sn$_{0.35}$Ti$_{0.07}$)O$_3$ antiferroelectric ceramics, and achieved a good energy storage performance: $W_{rec}$ and $\eta$ are of 7.63 J/cm$^3$ and 94% for $x = 0.45$ composition, respectively. Recently, Huang et al. [177] reported pure PHO ceramic films by sol–gel method at 650 °C annealing temperature, and achieved a $W_{rec}$ of 24.9 J/cm$^3$.

(2) (Pb, La)(Zr, Sn, Ti)O$_3$

As discussed in Section 3.2.1, Pb(Zr$_{1–x}$Ti$_x$)O$_3$ (PZT, $x \approx 0.05$) solid solutions located at rich Zr regions of ferroelectric–antiferroelectric (FE–AFE) phase boundary, exhibit rich phase structures and well electrical properties [61,62]. It is worth noting that PZT systems at FE–AFE phase boundary differ from MPB in electric properties. For instance, FE and AFE cannot be transformed into each other under force or electric field, while temperature, stress, or other factors induced by FE–AFE phase transition can occur. Meanwhile, the region of the antiferroelectric phase for PZT 95/5 is relatively narrow, and a slight composition fluctuation would easily cause deviation from FE–AFE phase boundary.

La$^{3+}$ and Sn$^{4+}$ are very popular A/B site dopants in PZT 95/5 ceramics where their functions are similar [178–182]. La$^{3+}$, as a donor dopant, substitutes Pb$^{2+}$ to disturb long-range ordering of domain by vacancy defect, which would strengthen the relaxor characteristic and expand the stabilized region of the antiferroelectric phase. Sn$^{4+}$ as an equal valence dopant of Ti$^{4+}$ functions not only expands the stabilized region of antiferroelectric, but also adjusts Zr/Ti ratio to enable Ti up to 10 mol%. Currently, the related works of stabilizing the Pb-based antiferroelectric phase mainly focus on adjusting suitable Zr/Sn/Ti ratio [183–185]. Liu et al. [186] found that $E_{A–F}$ linearly increased and the squareness of $P–E$ loop slightly improved when Ti content reduces from 0.11 to 0.07 mol at a fixed Zr of 0.58 mol. $W_{rec}$ enhances, thereby, from 0.28 to 2.35 J/cm$^3$ for Pb$_{0.97}$La$_{0.02}$(Zr$_{0.58}$Sn$_{0.35}$Ti$_{0.07}$)O$_3$ antiferroelectric ceramic bulks. In addition, it should be particularly noted that a high $W_{rec}$ is difficult to obtain when $E_{A–F}$ exceeds $E_b$.

In improving the breakdown behavior of Pb-based antiferroelectric ceramic bulks, Zhang et al. [187–189]
did a series of works using some special sintering technology. For instance, Zhang et al. [188] reported that 
\((\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02})(\text{Zr}_{0.68}\text{Sn}_{0.24}\text{Ti}_{0.08})\text{O}_3\) (PBLZST) ceramics using hot-press (HP) possessed a high \(W_{\text{rec}}\) of 3.2 J/cm\(^3\) at \(E_b = 180\) kV/cm due to smaller grain size and well insulation. Considering that special sintering technology requires expensive equipment, this method is not suitable for large-scale production. Some low-cost and convenient solutions are proposed, such as Bian et al. [190] used amorphous SiO\(_2\) to coat \(\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.33}\text{Sn}_{0.55}\text{Ti}_{0.12})\text{O}_3\) (PLZST), and measured a high \(W_{\text{rec}}\) of 2.68 J/cm\(^3\) due to \(E_b\) enhancing from 12.2 to 23.8 kV/mm. It should be noticed that the introduction of non-antiferroelectric phase will reduce the content of the original antiferroelectric phase, even that \(E_{\text{A–F}}\) would disappear.

In a physical method, Wang et al. [191] used a rolling process to enhance the mechanical strength of \((\text{Pb}_{0.98}\text{La}_{0.02})(\text{Zr}_{0.55}\text{Sn}_{0.45})_{0.995}\text{O}_3\) (PLZS) antiferroelectric ceramics. At 400 kV/cm, PLZS ceramics obtain a high \(W_{\text{rec}}\) of 10.4 J/cm\(^3\) and a \(\eta\) of 87%. Similarly, Zhang et al. [192] and Liu et al. [193] both utilized tape-casting method to fabricate antiferroelectric thick film. For example, Liu et al. [193] utilized tape-casting method to fabricate \((\text{Pb}_{0.98-x}\text{La}_{0.02}\text{Sr}_x)(\text{Zr}_{0.9}\text{Sn}_{0.1})_{0.995}\text{O}_3\) (PLSZS) antiferroelectric thick films, and achieved \(W_{\text{rec}}\) and \(\eta\) of 11.18 J/cm\(^3\) and 82.2% for \(x = 0.04\), respectively.

Due to the phase structure complexity of PZT-based ceramics near FE–AFE boundary, it usually displays different polarization behavior especially for ceramic films. Gao et al. [194] reported different oriented \((\text{Pb}_{0.98}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3\) (PLZT) thin films using PLD, obtained a \(W_{\text{rec}}\) of ~40 J/cm\(^3\) while \(\eta\) only of ~50% for (111) PLZT, which may be related to ferroelectric-like behavior (i.e., high \(P_r\)) under high electric field. Despite this condition, the combination of relaxor ferroelectric and antiferroelectric still receives more attention to enhance \(W_{\text{rec}}\). In addition, note that antiferroelectric behavior can be observed at different formulas such as PLZT at Zr/Ti \(\approx 52:48\) [196] or PLZST at Zr/(Sn+Ti) \(\approx 65:55\) [197]. With the development of micro-electric devices, flexible substrate such as Ti, Si, Ni foils, etc., is required to meet future application scenes. Ma et al. [195,198] did a series of meaningful works in the low-cost integration development of PLZT-based thin films. For instance, \(\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.95}\text{Ti}_{0.05}\) (PLZT 8/95/5) antiferroelectric ceramic films possess a high \(W_{\text{rec}}\) of 53 J/cm\(^3\) at mental foil by CSD, and effective work time would maintain 5000 h at room temperature [195]. Energy storage properties of Pb-based antiferroelectric ceramics and films are summarized and listed in Table 7.

### 3.3.2 Lead-free antiferroelectric ceramics

(1) NaNbO\(_3\)

NaNbO\(_3\) (NN) is a well-documented nonpolar antiferroelectric phase and possesses a complicated crystal structure due to the rotation of oxygen octahedron

| Composition | Category | \(t\) (nm) | \(W_{\text{rec}}\) (J/cm\(^3\)) | \(\eta\) (%) | \(c_r\) @ RT | \(E_b\) (kV/cm) | Ref. |
|-------------|----------|----------|----------------|----------|---------|--------|-----|
| PZ Thin film | 300–600 | 7.1 | — | 120–200 | [164] |
| PSZ5 Thin film | 500 | 14.5 | 78 | — | 150 | 900 | [165] |
| α-Fe\(_2\)O\(_3\) modified PZ Thin film | 660 | 17.4 | — | 600 | [169] |
| PZ:NiO Thin film | 140–170 | 24.6 | 58 | — | 600 | 1000 | [170] |
| Up-graded Eu-doped PZ Thin film | 400 | 16.3 | 67.4 | — | 300 | 1000 | [168] |
| PLHS Bulk | 0.11 mm | 7.63 | 94 | — | 280 | 380 | [176] |
| PHO Thin film | 330 | 24.9 | 73 | — | 2957 | [177] |
| PLZST 2/58/35/7 Bulk | 0.5 mm | 2.35 | 86.1 | — | 450 | 120 | [186] |
| PBLZST Bulk | 0.6 mm | 3.2 | — | — | 180 | [188] |
| PLZST 2/33/55/12 @5 mol\% SiO\(_2\) Bulk | 0.2 mm | 2.68 | — | — | 800 | 238 | [190] |
| PLZS Bulk | 0.11 mm | 10.4 | 87 | — | 180 | 400 | [191] |
| PLSZS Thick film | 0.1 mm | 11.18 | 82.2 | — | 200 | 400 | [193] |
| PLZT 2/95/5 Thin film | 300 | 40 | 53 | — | 1000 | [194] |
| PLZT 8/95/5 Thick film | 1 μm | 53 | — | — | 560 | 3500 | [195] |

Table 7: Energy storage properties of Pb-based antiferroelectric ceramic bulks and films

**Note:** PZ: PbZrO\(_3\); PSZ5: (Pb\(_{0.95}\text{Sr}_{0.05})\text{ZrO}_3\); PLHS: Pb\(_{0.98}\text{La}_{0.02}(\text{Hf}_{0.45}\text{Sn}_{0.55})_{0.995}\text{O}_3\); PHO: PbHfO\(_3\); PLZST: Pb\(_{0.98}\text{La}_{0.02}Zr\text{O}_3; PBLZST: (Pb\(_{0.98}\text{La}_{0.02})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3; PLZST 2/33/55/12: Pb\(_{0.98}\text{La}_{0.02}(Zr_{0.33}Sn_{0.55}Ti_{0.12})\text{O}_3; PLZST 2/95/5: Pb\(_{0.98}\text{La}_{0.02}Zr_{0.95}Ti_{0.05})\text{O}_3; PLZST 8/95/5: Pb\(_{0.98}Zr_{0.95}Ti_{0.05})O_3.

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and off-centered displacement of Nb$^{5+}$ [199,200]. In addition to temperature-induced transition, antiferroelectric–ferroelectric phase transition can also be induced by mechanical stress [201], grain size [202], and electric field [203]. Note that an electric field-induced antiferroelectric–ferroelectric phase transition is usually irreversible at room temperature because of the small free energy difference between antiferroelectric and ferroelectric.

Generally, reducing tolerance factor $t$ is still a widely accepted method to stabilize antiferroelectric phase of NN ceramics. For instance, Shimizu et al. [204] used CaZrO$_3$ (CZ), with similar electronegativity but smaller tolerance factor $t$, to modify NN ceramics. As the content of CZ increases, an obvious double $P$–$E$ loop accompanying to $E_{A-F}$ gradually increases while $P_{\text{max}}$ decreases, as shown in Fig. 13. Since then, other compounds such as SrZrO$_3$ (SZ) [205, CaHfO$_3$ (CH) [206], BiScO$_3$ (BS) [207], are both utilized to stabilize antiferroelectric phase, but few reports their energy storage performances. It should be pointed that double $P$–$E$ loop of NN-based ceramics still has more hysteresis loop at room temperature resulting in low $W_{\text{rec}}$. Moreover, Zhou et al. [208] firstly reported Bi$_2$O$_3$ modified NN energy storage ceramic bulks, obtained a high $W_{\text{rec}}$ of 4.03 J/cm$^3$ for Na$_{0.7}$Bi$_{0.1}$NbO$_3$ ceramics at $E_b = 250$ kV/cm attributed to the disrupted random electric field and reduced domain size. Energy storage properties of Na$_{0.7}$Bi$_{0.1}$NbO$_3$ system show good temperature stability (20–100 °C), fatigue endurance (10$^5$ cycles), and charge–discharge properties. After that, more Bi-based compounds including Bi(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (BMN) [209], Bi(Ni$_{1/2}$Sn$_{1/2}$)O$_3$ (BNS) [210], and so on, are used to improve the relaxor characteristics and acquire high $W_{\text{rec}}$. It is particularly important that $P$–$E$ loop of BiMeO$_3$ modified system becomes slimmer than pure NN ceramic, but characteristic double hysteresis loop fails to be observed.

A double $P$–$E$ hysteresis loop can be observed in high quality NN single crystal and ceramic film compared with ceramic bulk. However, a few studies reported energy storage properties of NN-based ceramic films, and concentrated on piezoelectric, dielectric tunability. In 2018, Fujii et al. [211] deposited 0.92NaNbO$_3$–0.08SrZrO$_3$ (0.92NN–0.08SZ) antiferroelectric thin films on SrRuO$_3$ buffered ST substrates with different orientations by using PLD. 0.92NN–0.08SZ thin films with (110) oriented substrate exhibit antiferroelectric behavior, while that with (001) oriented substrate is still ferroelectric. Recently, Beppu et al. [212] obtained $W_{\text{rec}}$ only of 2.9 J/cm$^3$ for 0.92NN–0.08SZ thin films at $E_b = 400$ kV/cm. In addition, Luo et al. [213] fabricated Mn-doped 0.96NaNbO$_3$–0.04CaZrO$_3$ (0.96NN–0.04CZ) thin films using sol–gel method, and leakage current of 1 mol% Mn reduces the magnitude of 10$^3$–10$^4$ compared to pure compositions. $W_{\text{rec}}$ and $\eta$ of 1 mol% Mn thin films are19.64 J/cm$^3$ and 64.5%, respectively. Nevertheless, simple composition and no toxic metal elements make it have broad prospects for energy storage research in the future.

(2) AgNbO$_3$

AgNbO$_3$ (AN) has a complicated phase structure and relatively low bandgap (~2.8 eV), and still has difficulty in observing double hysteresis loop at room temperature. Early studies of AN ceramics therefore concentrated on microwave communication and photocatalysis [214,215]. In addition, Ag$_2$O decomposition

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**Fig. 13** (a) Tolerance factor versus averaged electronegativity difference for (Na$_{1-x}$A$_{2x}$)($\text{Bi}_{1-x}$$\text{Nb}_{x}$)O$_3$ composition, where (A,B) = (Ca,Zr), (Ca,Hf), (Sr,Zr), and (Sr,Hf); (b) $P$–$E$ loops in the CZNN ceramics at 120 °C. Reproduced with permission from Ref. [204], © Royal Society of Chemistry 2015.
at a high temperature requires the fabrication of AN-based ceramics at the oxygen-rich environment. Similar to NN, AN-based ceramic bulk is a main research direction for energy storage capacitors.

In 2007, Fu et al. [216] successfully fabricated AN ceramics with a double hysteresis loop, and $P_{\text{max}}$ can up to 52 $\mu$C/cm$^2$ at 220 kV/cm exceeding other dielectric materials at the same electric field. The phenomenon strongly stimulates the studies of AN ceramics on energy storage applications. Tian et al. [217] synthesized pure AN antiferroelectric ceramic bulks, found two polarization structures by TEM and variable temperature $P$–$I$–$E$ loops, and attained a high $W_{\text{rec}}$ of 2.1 J/cm$^3$. In general, AN ceramics experience a series phase transition [218]:

$$M_1 \rightarrow M_2 \rightarrow M_3 \rightarrow O_1 \rightarrow O_2 \rightarrow T \rightarrow C$$

where $M_1$, $M_2$, and $M_3$ denote orthorhombic phases in rhombic orientation, $O_1$ and $O_2$ are the orthorhombic phases in a parallel orientation, while $T$ and $C$ denote the tetragonal and cubic phases, respectively. It is known that the stability of antiferroelectric phase of AN ceramic is closely related to phase transition among $M_1$, $M_2$, and $M_3$. Therefore, reducing phase transition temperature among $M_1$, $M_2$, and $M_3$ to low temperature would enhance $W_{\text{rec}}$ of AN-based ceramics [218–221].

Chemical doping is a simple and effective method to enhance $E_b$ due to an inverse relationship between $E_b$ and grain size. Recently, Wang et al. [228] synthesized AN ceramics using hydrothermal process, and obtained a maximum $E_b = 250$ kV/cm among pure AN ceramics so far. However, $P_{\text{max}}$ has an obvious decrease compared with other AN ceramics using solid-state method, and thus $W_{\text{rec}}$ and $\eta$ are only of 1.8 J/cm$^3$ and 40%, respectively. It is noteworthy that little attention has been shared on enhancing $E_b$ of AN ceramics by other different methods apart from ion-doping. Energy storage behaviors of NN and AN antiferroelectric ceramic bulks and films are summarized and listed in Table 8.

In summary, for antiferroelectric ceramics, tolerance factor $t$, electronegative difference, and polarizability are all influencing the stability of antiferroelectric phase. Note that the characteristic double $P$–$E$ loop of pure antiferroelectric phase is difficult to be observed, which needs to further explore the related reasons. Physical (special sintering technology, rolling process, etc.) and chemical (coating, hydrothermal process, etc.) methods can enhance $E_b$ by improving sintering behavior or mechanical strength.

![Fig. 14](https://example.com/fig14.png)

**Fig. 14** (a) $P$–$E$ loops of AgNbO$_3$ and Ag(Nb$_{0.85}$Ta$_{0.15}$)O$_3$ ceramic; (b) energy storage performances of Ag(Nb$_{1-x}$Ta$_x$)O$_3$ ceramics prior to their breakdown. Reproduced with permission from Ref. [218], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2017.
Table 8  Energy storage properties of NN and AN-based antiferroelectric ceramic bulks and films

| Composition      | Category | $t$ (μm) | $W_{rec}$ (J/cm³) | $\eta$ (%) | $\varepsilon_r$ @ RT | $E_b$ (kV/cm) | Ref. |
|------------------|----------|----------|-------------------|------------|----------------------|---------------|------|
| Na$_{0.7}$Bi$_{0.1}$NbO$_3$ Bulk | 0.2 mm | 3.44 | 85.4 | $-1700$ | 351 | [208] |
| 0.92NN–0.08SZ Thick film | 1 μm  | 2.9 | 67 | 211 | 400 | [212] |
| 1 mol% Mn-doped 0.96NN–0.04CZ Thin film | 300 nm | 19.64 | 64.5 | $-2200$ | 833.3 | [213] |
| AN Bulk | 0.5 mm | 2.1 | — | $-300$ | 175 | [217] |
| ANT15 Bulk | 200 μm | 4.2 | 69 | $-200$ | 233 | [218] |
| AN | 150 μm | $-1.8$ | $-40$ | $-80$ | 250 | [228] |

NN: NaNbO$_3$; SZ: SrZrO$_3$; CZ: CaZrO$_3$; AN: AgNbO$_3$; ANT15: Ag(Nb$_{0.85}$Ta$_{0.15}$)O$_3$.

4 Conclusions and perspectives

From the perspectives of composition modification, structural design, and electrical performance optimization, this paper briefly compares the research progress of energy storage ceramic bulks and films. Currently, $W_{rec}$ of ceramic bulks is generally less than 10 J/cm³, while that of films can reach 10$^2$ J/cm³. Except for ceramic composition, $W_{rec}$ is also closely related to other factors such as sample thickness, preparation, and testing methods. Although giant $\varepsilon_r$ linear dielectric attracts more attention, it may be not suitable for energy storage capacitors. In contrast, relaxor ferroelectric and antiferroelectric with high $P_{max}$ and low $P_r$ are easier to obtain high $W_{rec}$ than linear dielectric, so they are relatively ideal energy storage dielectric materials. Whether for bulks or films, $E_b$ is a decisive factor for affecting the upper limit of $W_{rec}$. In addition, the development from material to device still has a large gap, and thus needs to make more efforts to solve this problem. Judging from the existing researches, the authors believe that the following aspects need further exploration and improvement:

1) It is still a long process to select the ideal energy storage ceramics through a single experiment. If relevant predictions and screenings can be combined with theoretical calculations or machine learning methods, work efficiency will be greatly improved.

2) In order to better understand the variation in domain and phase structures as functions of the electric field, thermal, force, magnetic, etc., external fields, in-situ observation technique would be an important direction, which would help us to comprehensively understand the microscopic evolution mechanism of polarization.

3) For materials with crystalline/amorphous phase and multilayer structure, the issues of generation reason and corresponding mechanisms of interface behaviors (such as interface polarization, fatigue, etc.) and stress still need to be deeply investigated.

4) Considering many factors to influence $W_{rec}$ and $\eta$, it is important to standardize the test parameters such as sample thickness, area of electrode, testing frequency, and AC/DC conditions, and establish the relevant test standard for performance evaluation of energy storage materials.

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