Progress and perspectives in dielectric energy storage ceramics

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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 ($\geq 10^6$ cycles), and high temperature stability, playing an

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Fig. 1 Ragone pattern of different energy storage technologies.

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 (ϵ_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 ($P_{\max}$), 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 ($> 100 \mu\text{m}$), thick film ($1\text{--}100 \mu\text{m}$), and thin film ($< 1 \mu\text{m}$). 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]:

$$W = \int_0^{D_{\max}} E dD \quad (1)$$

where W , E , $D_{\max}$, 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:

$$D = \epsilon_0 E + P \quad (2)$$

Meanwhile, P is dependent on E as follows:

$$P = \epsilon_0 \chi E \quad (3)$$

where ϵ_0 is the vacuum dielectric constant of $8.854 \times 10^{-12} \text{ F/m}$, χ is the dielectric polarization coefficient, so

Fig. 2 Typical dependence of polarization and permittivity on electric field for (a) linear dielectric, (b) relaxor ferroelectric, and (c) antiferroelectric. Reproduced with permission from Ref. [2], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2017.

that Eq. (2) can be expressed as

$$D = \varepsilon_0(\chi + 1)E = \varepsilon_0\varepsilon_r(E)E \quad (4)$$

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

$$W = \int_0^{E_{\max}} \varepsilon_0\varepsilon_r(E)EdE \quad (5)$$

It is obvious that high ε_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_{rec}) and energy loss (W_{loss}) [8,11]. In practice, W_{rec} is more important than W in evaluating the energy storage performances of dielectric materials. As shown in Fig. 2, W_{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:

$$W_{\text{rec}} = \int_{P_r}^{P_{\max}} EdP \quad (6)$$

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

2.2 Energy storage efficiency

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

$$\eta = \frac{W_{\text{rec}}}{W} \times 100\% = \frac{W_{\text{rec}}}{W_{\text{rec}} + W_{\text{loss}}} \times 100\% \quad (7)$$

where W_{loss} is the energy loss during the discharge process, which equals to the area enclosed by the P – E loop in number. W_{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 η , and then improve its practical application.

According to Eqs. (6) and (7), P – E loops go slim accompanied with high $P_{\max}$, low P_r (i.e., high $\Delta P = P_{\max} - P_r$), 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 (Φ) 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

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

where φ is the effective volume, τ 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_{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_{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:

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

where f is the testing frequency, and the others are the same as those discussed above. It can be seen that high ε_r , high E_b , and low $\tan \delta$ are the basic requirements of

Fig. 3 (a) Circuit of charging–discharging. (b) Discharging current (I) and energy density (J) versus time. Reproduced with permission from Ref. [1], © Elsevier Ltd. 2018.

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 $\pm 15\%$ 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 multi-functional 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 ϵ_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 ϵ_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 TiO_2 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 TiO_2 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 $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics from extrinsic factors influencing dielectric constant. Actually, most of subsequent discussion on the physical origin of different-type donor/acceptor co-doped TiO_2 ceramics is basically around above two mechanisms [26–28], even though no significant progress has been achieved in W_{rec} for donor/acceptor co-doping TiO_2 ceramics because of the expense of a rapid reduction in E_b .

In another way, improving the sintering behavior of TiO_2 -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_{rec} of 1.15 J/cm^3 for alkali-free glass modified TiO_2 ceramics at 501.7 kV/cm . Unfortunately, W_{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 TiO_2 film is a good direction owing to their high E_b . For instance, Chao and Dogan [31] fabricated 0.1-mm thick TiO_2 films using tape-casting method, which achieve W_{rec} of 14 J/cm^3 at 1400 kV/cm .

3.1.2 SrTiO_3 based ceramics

SrTiO_3 (ST) is a cubic paraelectric phase with ABO_3 type perovskite structure, accompanying to space group of $Pm\bar{3}m$ and lattice constant of $a = 3.905 \text{ \AA}$ [32,33]. ST ceramics possess moderate ϵ_r of ~ 300 , E_b of $\sim 100 \text{ kV/cm}$, and low $\tan\delta$ of $\sim 10^{-3}$, 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 TiO_2 ceramic (~ 110) and polymer linear dielectric (< 10), ST has an advantage of relatively high ϵ_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 SrTiO_3 and high ϵ_r of BaTiO_3 , 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 $\sim 393 \text{ K}$. 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_{rec} , while relatively low and rapidly decreased η becomes a serious problem to hinder its application. By comparison, $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ possessed moderate W_{rec} , high η ($\geq 95\%$), 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.

For aliovalent doping in A-site of ST, a similar phenomenon with giant dielectric TiO_2 can be observed, and corresponding mechanisms are widely studied. Chen *et al.* [41–43] reported $(\text{Bi},\text{Sr})\text{TiO}_3$ 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 ($\text{Re}^{3+} = \text{La}, \text{Sm}, \text{Gd}, \text{Er}, \text{Nd}, \text{etc.}$) to replace Sr^{2+} , 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 $\text{Re}_{0.02}\text{Sr}_{0.97}\text{TiO}_3$ 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 $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ ceramics with various grain

Fig. 5 ϵ_r and $\tan\delta$ of the $\text{Re}_{0.02}\text{Sr}_{0.97}\text{TiO}_3$ ceramics as a function of measuring temperature from -60 to 200 °C. Reproduced with permission from Ref. [44], © The American Ceramic Society 2013.

Fig. 6 ϵ_r of the $\text{Re}_{0.02}\text{Sr}_{0.97}\text{TiO}_3$ ceramics as a function of bias electric field. Filled pattern: increasing bias. Open pattern: decreasing bias. Reproduced with permission from Ref. [44], © The American Ceramic Society 2013.

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). $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ ceramic bulk with grain size of 0.5 μm achieves a high $W_{\text{rec}} = 1.28$ J/cm^3 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) $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ 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/cm^3 at $E_b = 230$ kV/cm , which is approximately twice as much as that of CS samples (0.57 J/cm^3). 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 $(\text{Sr}_{1-1.5x}\text{Bi}_x)\text{Ti}_{0.99}\text{Mn}_{0.01}\text{O}_3$ (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 (TiO_6) octahedra induced by the formation of $\text{Bi}^{3+}-\text{V}_{\text{Sr}}''$ defect complex. Under an electric field of 1982 kV/cm ,

($\text{Sr}_{0.85}\text{Bi}_{0.1}\text{Ti}_{0.99}\text{Mn}_{0.01}\text{O}_3$) possess a W_{rec} of 24.4 J/cm^3 accompanied by the largest ΔP ($P_{\text{max}} - P_{\text{r}} = 34.3 \mu\text{C/cm}^2$). Actually, the introduction of other Bi-contained compounds such as $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (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_{rec} and η 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 2×10^7 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_{max} (up to $10^2 \mu\text{C/cm}^2$) along the positive direction were higher than the negative direction. Therefore, a maximum W_{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 ε_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_{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_2O_3 as a blocking layer to form heterostructure, and achieved a maximum W_{rec} of 39.49 J/cm^3 at $E_b = 7542.3 \text{ kV/cm}$ when interface number equals 4. Recently, Chen *et al.* [58] used $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_{1.8}$ (CSZ) as dead layer to enhance E_b of $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{Zr}_{0.18}\text{Ti}_{0.82}\text{O}_3$ (BSZT) thin films. Due to the formation of a high electron injection barrier, Schottky electron emission is suppressed, and thus E_b and W_{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	$W_{\text{rec}} (\text{J/cm}^3)$	$\eta (\%)$	$\varepsilon_r @ \text{RT}$	$E_b (\text{kV/cm})$	Ref.
$\text{TiO}_2 + 15 \text{ wt\% BBAS}$	Bulk	—	1.15	—	103	501.7	[30]
TiO_2	Thick film	0.1 mm	14	—	108	1400	[31]
$\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$	Bulk	0.6 mm	0.23	95.7	650	~90	[37]
$\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$	Bulk	0.3 mm	1.28	—	~1500	243	[47]
$\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ (SPS)	Bulk	—	1.13	86.8	—	230	[48]
$(\text{Sr}_{0.85}\text{Bi}_{0.1})\text{Ti}_{0.99}\text{Mn}_{0.01}\text{O}_3$	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_2O_3 – Al_2O_3 – SiO_2 ; ST: SrTiO_3 ; BF: BiFeO_3 ; AO: Al_2O_3 ; BSZT: $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{Zr}_{0.18}\text{Ti}_{0.82}\text{O}_3$.

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 $P_{\max}$ while its high P_r leads to that most of energy is dissipated during the discharge process. By contrast, relaxor ferroelectric exhibits slim P – E loop with high $P_{\max}$ and low P_r (i.e., high $\Delta P = P_{\max} - P_r$) 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_{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 $(\text{Pb}_{0.89}\text{La}_{0.11})(\text{Zr}_{0.70}\text{Ti}_{0.30})_{0.9725}\text{O}_3$ (PLZT 11/70/30) ceramics

achieved a W_{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 $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ -based thin films, acquired a high $W_{\text{rec}} = 28.2 \text{ J/cm}^3$ for $\text{PbZrO}_3/\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ bilayer thin films at 2410 kV/cm. In addition, they continued to design a sandwich structure of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3/\text{Al}_2\text{O}_3/\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (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_{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_r 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]. $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ (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 $\text{Ti}/(\text{Zr}+\text{Ti})$ ratio gradually increases, ϵ_r enhances while $\tan\delta$ shows an opposite trend indicating phase structure gradually transforms from relaxor ferroelectric into normal ferroelectric. At $E_b = 2180 \text{ kV/cm}$, W_{rec} , η 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 $(\text{Pb}_{0.91}\text{La}_{0.09})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (PLZT 9/65/35) to enlarge the polarization difference of $P_{\max} - P_r$, measured a W_{rec} of 30.8 J/cm^3 for 1 mol% Mn

Fig. 7 Schematic of hysteresis loop: (a) normal ferroelectric and (b) relaxor ferroelectric.

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 $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (PLZT, $x = 0.08, 0.09, 0.1$) thick films using sol-gel method. Up-graded PLZT films possess a W_{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 $(\text{Pb}_{0.9}\text{La}_{0.1})(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PLZT 10/52/48) thin films using PLD on Si substrate choosing $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ (CNOs) and $\text{Ti}_{0.87}\text{O}_2$ (TiOns) nanosheets as the template layer. Highly textured (001)-oriented PLZT 10/52/48 films grown on CNOs possess a high W_{rec} of

58.4 J/cm^3 , which exceeds W_{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 $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.905}\text{Sn}_{0.015}\text{Ti}_{0.08})\text{O}_3$ (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”. E_b and W_{rec} at room temperature are greatly enhanced (nearly doubled) from 1286 to 2000 kV/cm , and from 16.6 to 31.2 J/cm^3 , respectively. Energy storage performances of Pb-based relaxor ferroelectric materials are summarized and listed in Table 2.

Fig. 8 (a) P - E loops of the PLZT films on different substrates. Reproduced with permission from Ref. [69], © Springer Science Business Media New York 2015. (b) P - E loops of the $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.905}\text{Sn}_{0.015}\text{Ti}_{0.08})\text{O}_3$ 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.

Table 2 Energy storage properties of Pb-based relaxor ferroelectric ceramic bulks and films

Composition	Category	t	$W_{\text{rec}} (\text{J/cm}^3)$	η (%)	ε_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	$1.5 \mu\text{m}$	30.8	~70	1378	1679	[74]
Up-graded PLZT	Thick film	$1.5 \mu\text{m}$	12.4	—	2170	800	[76]
PLZT 10/52/48	Thick film	1000 nm	58.4	81.2	—	3400	[77]
PLZT	Thick film	~2 μm	85	65	~1300	~2600	[69]
Low-temperature-poling PLZST	Thin film	320–350 nm	31.2	60	—	2000	[70]

PZ/PZT 52/48: $\text{PbZrO}_3/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$; PZT/AO/PZT: $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3/\text{Al}_2\text{O}_3/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$; PLZT 8/52/48: $\text{Pb}_{0.92}\text{La}_{0.08}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$; PLZT 9/65/35: $(\text{Pb}_{0.91}\text{La}_{0.09})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$; up-graded PLZT: $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ ($x = 0.08, 0.09, \text{ and } 0.10$); PLZT 10/52/48: $\text{Pb}_{0.9}\text{La}_{0.1}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$; PLZST: $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.905}\text{Sn}_{0.015}\text{Ti}_{0.08})\text{O}_3$.

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 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT), BaTiO_3 (BT), BiFeO_3 (BF), and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) systems, which will be discussed in the following sections.

(1) $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ based ceramics

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (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_{max} ($\sim 40 \mu\text{C}/\text{cm}^2$) [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 ($\sim 38 \mu\text{C}/\text{cm}^2$), high E_c ($\sim 73 \text{ kV}/\text{cm}$), and poor sintering behavior for pure BNT ceramics hinder its energy storage applications.

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – $x\text{BaTiO}_3$ ($x = 6\%$ – 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_{rec} . In 2011, Gao *et al.* [90] firstly reported that $0.89\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – 0.06BaTiO_3 – $0.05\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (0.89BNT – 0.06BT – 0.05KNN) ceramics possessed a W_{rec} of $0.46 \text{ J}/\text{cm}^3$ at $56 \text{ kV}/\text{cm}$. In 2016, Cao *et al.* [91] used Mn^{2+} to modify $0.7(0.94\text{BNT}$ – $0.06\text{BT})$ – 0.3ST ceramics to reduce P_r by forming Mn_{Ti}'' – $\text{V}_{\text{O}}^\bullet$ defect complex, which can induce a local electric field influencing domain switch. A W_{rec} of $1.06 \text{ J}/\text{cm}^3$ for $1.1 \text{ mol}\%$ Mn is obtained at $95 \text{ kV}/\text{cm}$ owing to a large P_{max} – P_r up to $36.8 \mu\text{C}/\text{cm}^2$. Actually, similar phenomenon was already reported by Ren *et al.* [92]. In 2017, Li *et al.* [93] incorporated NaNbO_3 into $0.8\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – 0.2SrTiO_3 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 NaNbO_3 modified ceramics exhibit a high W_{rec} of $0.74 \text{ J}/\text{cm}^3$, 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_{rec} [94]. In our previous work [37,95], $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$, 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 ϵ_r ($\text{Ba}_{0.3}\text{Sr}_{0.7}$) $_{0.35}(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.65}\text{TiO}_3$ ($\text{BS}_{0.35}\text{BNT}$) 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_xBNT ceramics. The inset is T_m as a function of x value. (b) P – E hysteresis loops of the BS_xBNT 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]. 0.94BSBT–0.06NN relaxor ferroelectric ceramics achieve a high W_{rec} of 1.25 J/cm³ 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)Bi_{0.5}Na_{0.5}TiO₃– x (Sr_{0.7}Bi_{0.2})TiO₃ (NBT– x SBT, $x = 0.3$ – 0.5) ceramics, and corresponding multilayer ceramic capacitors (MLCC) with a single layer thickness of 20 μm were fabricated. A high W_{rec} of 9.5 J/cm³, together with η 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_b 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)/(0.93Bi_{0.5}Na_{0.5}TiO₃–0.07Ba_{0.94}La_{0.04}Zr_{0.02}Ti_{0.98}O₃) (STL/(BNT–BLZT)) ceramics along thickness direction. A high W_{rec} of 2.72 J/cm³ 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 or even 300 °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 metal 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 $\text{Mn}_{\text{Ti}}'' - \text{V}_{\text{O}}^\bullet$ defect complex, which gives rise to a W_{rec} of 30.2 J/cm³ 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_{max} can reach to 10² $\mu\text{C}/\text{cm}^2$ scale due to the complicated phase composition and great relaxor dispersion. (100) and (111) oriented (Bi_{1/2}Na_{1/2})_{0.9118}La_{0.02}Ba_{0.0582}(Ti_{0.97}Zr_{0.03})O₃ (BNLBTZ) thin films achieve maximum W_{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.* [108] reported the introduction of Bi_{3.25}La_{0.75}Ti₃O₁₂ (BLT) and Pb(Zr_{0.4}Ti_{0.6})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(Bi_{0.5}Na_{0.5})TiO₃–0.06BaTiO₃/BiFeO₃ (abbreviated as BNBT/*n*BFO) multilayer film capacitors under a given total thickness. BNBT/2BF thin films exhibit a W_{rec} of 31.96 J/cm³ and a η 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 (Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO₃/0.6(Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO₃–0.4SrTiO₃ (NKBT/NKBT–ST)_{*N*} ($N = 2, 3, 6, 8$) films on the F-Mica substrate, with measured W_{rec} of 73.7 J/cm³ 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 ϵ_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

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

Composition	Category	t	W_{rec} (J/cm ³)	η (%)	ϵ_r @ RT	E_b (kV/cm)	Ref.
0.89BNT–0.06BT–0.05KNN	Bulk	0.5 mm	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(0.8BNT–0.2ST)–0.05NN	Bulk	—	0.74	55	~2000	70	[93]
0.94BS _{0.35} BNT–0.06NN	Bulk	0.3–0.35 mm	1.25	76	~3800	116	[96]
0.55BNT–0.45SBT	Bulk	20 μm @ SL	9.5	92	~2500	720	[15]
STL/(BNT–BLTZ)	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	~500	2400	[106]
(NKBT/NKBT–ST) _{N=6}	Thin film	260 nm	73.7	68.1	~600	3072	[107]

BNT: Bi_{0.5}Na_{0.5}TiO₃; BT: BaTiO₃; KNN: K_{0.5}Na_{0.5}NbO₃; ST: SrTiO₃; NN: NaNbO₃; BS_{0.35}BNT: (Ba_{0.3}Sr_{0.7})_{0.35}(Bi_{0.5}Na_{0.5})_{0.65}TiO₃; SBT: Sr_{0.7}Bi_{0.2}TiO₃; STL/(BNT–BLTZ): (SrTiO₃ + 0.5 wt% Li₂CO₃)/(0.93Bi_{0.5}Na_{0.5}TiO₃–0.07Ba_{0.94}La_{0.04}Zr_{0.02}Ti_{0.98}O₃); BNLBTZ: (Bi_{1/2}Na_{1/2})_{0.9118}La_{0.02}Ba_{0.0582}(Ti_{0.97}Zr_{0.03})O₃; BF: BiFeO₃; NKBT: (Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO₃. SL means single layer.

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_r , the reduction from Ti⁴⁺ to Ti³⁺ at high temperature, which restrict it to achieve high W_{rec} [114].

In 2009, Ogihara *et al.* [115] synthesized a temperature stable 0.7BaTiO₃–0.3BiScO₃ (0.7BT–0.3BS) relaxor ferroelectric ceramics with a thickness of 0.2 mm, and obtained W_{rec} of 2.3 J/cm³ at 225 kV/cm. When thickness reduces to 15 μm , W_{rec} enhances to 6.1 J/cm³ at 730 kV/cm. By comparison, Wu *et al.* [116] utilized BiScO₃ (BS) as shell material to coat BT, and W_{rec} only of 0.68 J/cm³ 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})O₃ (BMZ) modified BT-based relaxor ferroelectric, and achieved a high W_{rec} = 2.9 J/cm³ for 0.85BT–0.15BMZ ceramics higher than pure BT ceramics (0.4 J/cm³), and corresponding P – E loop is exhibited in Fig. 10(a). The authors thought the enhancement of W_{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 BaTiO₃–Bi(Mg,Ti)O₃ (BT–BMT) also display good energy storage capabilities due to the low tolerance factor of Bi-based compound [118,119]. In recent years, Ba_{0.85}Ca_{0.15}Zr_{0.10}Ti_{0.90}O₃ (BCZT) based relaxor ferroelectric gains more attention in ferroelectric and pyroelectric properties because of high ϵ_r at room temperature [120–123]. However, W_{rec} of BCZT-based ceramic bulks is commonly less than 3 J/cm³ limited to a low E_b . If the trade-off relationship between ϵ_r and E_b

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–20B₂O₃–15SiO₂ and 65Bi₂O₃–20B₂O₃–15SiO₂ glass phases, reducing sintering temperature to 900 °C. Meanwhile, the authors estimated W_{rec} approaching to 10 J/cm³ by equation for Bi-based glass phase. Similarly, high E_b materials such as SiO₂ [125] and SrTiO₃ (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_{rec} only of 0.22 J/cm³ at 47 kV/cm, η approaches to 90%. It should be pointed that high E_b materials usually possess low ϵ_r , and so W_{rec} of coated BT ceramics cannot be effectively enhanced at the sacrifice of ϵ_r . Bi-based materials such as BiScO₃ as shell material also suffer from the same problem of obtaining high W_{rec} . The reason needs to be further explored due to the complex composition gradient.

Ba(Zr,Ti)O₃ (BZT) based ceramic films are considered to be a potential energy storage material since Zr⁴⁺ has a stable valence and similar ion radius of Ti⁴⁺, as well as good relaxor characteristics. As Zr⁴⁺ content increases, relaxor degree gradually enhances, and a weak diffuse phase transition accompanying slim P – E loop can be founded when Zr⁴⁺ near 15 mol%, which is attributed to the inhomogeneous distribution of Zr and mechanical stress [128,129]. Therefore, energy

Fig. 10 (a) P - E loop of $\text{BaTiO}_3\text{-}x\text{Bi}(\text{Mg}_{1/2}\text{Zr}_{1/2})\text{O}_3$ at room temperature. Reproduced with permission from Ref. [117], © Elsevier Ltd. 2018. (b) EDS line scanning analysis of Sr in the BT@ST ceramic. Reproduced with permission from Ref. [126], © The Royal Society of Chemistry 2015. (c) Schematic of the microstructure evolution with film thickness for $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ thin films. Reproduced with permission from Ref. [127], © The Author(s) 2017.

storage performances of BZT-based ceramic systems receive more attention. Instan *et al.* [130] prepared 400 nm $\langle 100 \rangle$ -oriented $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($x = 0.3, 0.4, 0.5$) relaxor ferroelectric thin films using PLD on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{MgO}$ 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 $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ 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 $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ 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 $\text{BaTiO}_3/\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ 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

$W_{\text{rec}} = 46 \text{ J/cm}^3$ at E_b reach to 5.8–6 MV/cm. Sun *et al.* [133] studied energy storage properties of laminated $\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3/\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (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) BiFeO₃-based ceramics

BiFeO₃ (BF) as a multiferroic material with perovskite structure exhibits high T_C ($\sim 850^\circ\text{C}$), high P_s ($\sim 100 \mu\text{C/cm}^2$), and large S_{max} ($\sim 0.4\%$), 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	W_{rec} (J/cm ³)	η (%)	ϵ_r @ RT	E_b (kV/cm)	Ref.
0.7BT–0.3BS	Bulk	0.2 mm	2.3	—	~900	225	[115]
	Thick film	15 μm	6.1	—	750–800	730	
BT@3BS	Bulk	—	0.68	81	~1500	120	[116]
0.85BT–0.15BMZ	Bulk	0.2 mm	2.9	86.8	~1000	279.8	[117]
BT with BBS glass	Bulk	—	~10	—	~550	~1140	[124]
BT@ST	Bulk	—	0.22	~90	~2000	47	[126]
<100>-oriented Ba(Zr _{0.3} Ti _{0.7})O ₃	Thin film	400 nm	156 $\pm$ 1	72.8	~3400	3000	[130]
Ba(Zr _{0.2} Ti _{0.8})O ₃	Thin film	350 nm	166	~90	~350	5700	[127]
Superlattice BT/BST	Thin film	0.6 μm	~12.24	—	~800	1660	[132]
(BCT/BZT) _{N=8}	Thin film	100 nm	52.4	72.3	~175	4700	[133]

BT: BaTiO₃; BS: BiScO₃; BMZ: Bi(Mg_{1/2}Zr_{1/2})O₃; BBS: 65Bi₂O₃–20B₂O₃–15SiO₂; ST: SrTiO₃; BST: Ba_{0.3}Sr_{0.7}TiO₃; BCT: Ba_{0.7}Ca_{0.3}TiO₃; BZT: BaZr_{0.2}Ti_{0.8}O₃.

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

BiFeO₃– x BaTiO₃ (BF– x BT, $0 \leq x \leq 0.5$) ceramics maintain high T_C , good ferroelectric and piezoelectric properties resulted from complicated phase structure evolution. With increasing x value, BF– x BT ceramics possess a high P_{max} 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 P_r . For example, Liu *et al.* [144] added Ba(Zn_{1/3}Ta_{2/3})O₃ (BZT) into BT–0.34BT relaxor ferroelectric ceramics obtaining a W_{rec} 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 E_b is given in

Fig. 11(a). At 360 kV/cm, $x = 0.1$ sample possesses a maximum W_{rec} 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 W_{rec} of 0.62BF–0.3BT–0.08Nd(Zr_{0.5}Zn_{0.5})O₃ ceramic bulks is 2.45 J/cm³ at 240 kV/cm. When an MLCC device based on this system is made, W_{rec} is enhanced to 10.5 J/cm³.

Similar to BF– x BT 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 W_{rec} of 18.6 J/cm³ at 972 kV/cm. Recently, Pan *et al.* [148] reported (0.55– x)BF– x BT–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 (a) Weibull distribution and calculated E_b values of (0.67– x)BF–0.33BT– x NN 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.

$W_{\text{rec}} = 112 \text{ J/cm}^3$ more than 53 J/cm^3 of pure 0.55BF–0.45ST thin films, which is owing to the enhanced relaxor behaviors and breakdown strengthen. Moreover, the energy storage performances of this system maintain good stability in a wide temperature range of $(-100)–150^\circ\text{C}$ and 10^8 cycles, respectively. In addition, an important and interesting double P – E loop can be observed in rare earth substituted BF thin films due to the transition from orthorhombic to rhombohedral phase [149].

In heterostructure design, McMillen *et al.* [150] firstly proposed to use “artificial dead layer” to enhance E_b , deposited Al_2O_3 layer with 6 nm between 0.6BF–0.4ST film and ST substrate, and corresponding P – E loops before and after inserting Al_2O_3 layer were illustrated in Fig. 11(b). Interface polarization behavior to some degree increases hysteresis loss while Al_2O_3 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) $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ -based ceramics

$\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) is a binary solid solution of KNbO_3 ferroelectric and NaNbO_3 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 KNbO_3 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 SrTiO_3 (ST) [155] and $\text{Bi}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (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% BiFeO_3 -doped $(\text{K}_{0.5}\text{Na}_{0.5})(\text{Mn}_{0.005}\text{Nb}_{0.995})\text{O}_3$ (KNMN) thick film possessed a slim P – E loop, and achieved a W_{rec} of 28 J/cm^3 , η of 90.3%. Recently, Huang *et al.* [161] also used MnO_2 to reduce leakage current of $0.95(\text{K}_{0.49}\text{Na}_{0.49}\text{Li}_{0.02})(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_3$ –0.05 CaZrO_3 – x mol% Mn (KNN–LT–CZ5– x mol% Mn) thin films prepared by sol–gel methods, and achieved a high $W_{\text{rec}} = 64.6 \text{ J/cm}^3$ 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

Table 5 Energy storage properties of BF-based relaxor ferroelectric ceramic bulks and films

Composition	Category	t	$W_{\text{rec}} (\text{J/cm}^3)$	η (%)	ε_r @ RT	E_b (kV/cm)	Ref.
0.6BF–0.34BT–0.06BZT	Bulk	0.2 mm	2.56	~ 70	—	160	[144]
0.57BF–0.33BT–0.1NN	Bulk	0.15 mm	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	~ 900	972	[147]
0.25BF–0.3BT–0.45ST	Thin film	450–500 nm	112	80	~ 250	4900	[148]
Dead layer engineered 0.6BF–0.4ST	Thin film	400 nm	17	—	—	—	[150]

BF: BiFeO_3 ; BT: BaTiO_3 ; BZT: $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$; NN: NaNbO_3 ; NZZ: $\text{Nd}(\text{Zn}_{0.5}\text{Zr}_{0.5})\text{O}_3$; ST: SrTiO_3 . SL means single layer.

Table 6 Energy storage properties of KNN-based relaxor ferroelectric ceramic bulks and films

Composition	Category	t	W_{rec} (J/cm ³)	η (%)	ε_r @ RT	E_b (kV/cm)	Ref.
0.85KNN–0.15ST	Bulk	0.2 mm	4.03	~52	~1500	400	[155]
0.90KNN–0.10BMN	Bulk	0.2 mm	4.08	62.7	~1000	300	[156]
BiFeO ₃ -doped KNMN	Thick film	1 μ m	28	90.3	—	2000	[160]
5 mol% Mn-doped KNN–LT–CZ5	Thin film	650 nm	64.6	84.6	—	3080	[161]

ST: SrTiO₃; BMN: Bi(Mg_{2/3}Nb_{1/3})O₃; KNMN: (K_{0.5}Na_{0.5})(Mn_{0.005}Nb_{0.995})O₃; KNN–LT–CZ5: 0.95(K_{0.49}Na_{0.49}Li_{0.02})(Nb_{0.8}Ta_{0.2})O₃–0.05CaZrO₃

slim. In addition, delay saturated polarization is also used to optimize polarization behavior. Designing multilayer ceramic capacitor (MLCC), “core–shell” structure with non-ferroelectric phase as shell material is commonly accepted method to improve electric breakdown behavior for ceramic bulks. By comparison, chemical modification of ceramic films functions two 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 parameters 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_s in a unit cell, but the direction of P_s 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_{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, $E = 0$, $P_r = 0$). 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_{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_b has become a particularly important issue to acquire good energy storage performances.

3.3.1 Pb-based antiferroelectric ceramics

(1) PbZrO₃

PbZrO₃ (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_{max} and low P_r makes it suitable for energy storage capacitors. PZ-based energy storage ceramics gain increasing attention since Chen *et al.* [164] reported W_{rec} of 7.1 J/cm³ 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 Pb²⁺ (1.20 Å) with smaller Sr²⁺ (1.12 Å) to reduce t , and P – E loop goes slim together with increased E_{A-F} and decreased ΔE . As a consequence, (Pb_{0.95}Sr_{0.05})ZrO₃ (PSZ5) thin films obtain a W_{rec} of

14.5 J/cm³. Choosing smaller ion radius while aliovalent of La³⁺ 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 $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles to modify PZ thin films, obtained a W_{rec} of 17.4 J/cm³ and P_{max} as high as 78 $\mu\text{C}/\text{cm}^2$ 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 $E_b = 1000$ kV/cm, 5 vol% NiO thin films possess a high P_{max} of ~ 91 $\mu\text{C}/\text{cm}^2$, and W_{rec} of 24.6 J/cm³. Meanwhile, Ge *et al.* [171,172] also did a series of works on optimizing polarization behavior mainly such as enhancing P_{max} , reducing $E_{\text{A-F}}-E_{\text{F-A}}$ 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/cm³ for down-graded higher than that of 9.7 J/cm³ for up-graded PZ-based thin films, and corresponding P – E loops are shown in Fig. 12.

Fig. 12 P – E loops of up- and down-graded Eu-doped PZ thin films. Inset: the differentiated P – E hysteresis loops of down- and up-graded thin films, respectively. Reproduced with permission from Ref. [168], © The American Ceramic Society 2012.

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 $\text{Pb}_{0.98}\text{La}_{0.02}(\text{Hf}_x\text{Sn}_{1-x})_{0.995}\text{O}_3$ antiferroelectric ceramics, and achieved a good energy storage performance: W_{rec} and η are of 7.63 J/cm³ 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/cm³.

(2) (Pb, La)(Zr, Sn, Ti)O₃

As discussed in Section 3.2.1, $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (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.

La³⁺ and Sn⁴⁺ are very popular A/B site dopants in PZT 95/5 ceramics where their functions are similar [178–182]. La³⁺, 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. Sn⁴⁺ as an equal valence dopant of Ti⁴⁺ 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 $E_{\text{A-F}}$ 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/cm³ for $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.58}\text{Sn}_{0.35}\text{Ti}_{0.07})\text{O}_3$ antiferroelectric ceramic bulks. In addition, it should be particularly noted that a high W_{rec} is difficult to obtain when $E_{\text{A-F}}$ 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_{rec} of 3.2 J/cm^3 at $E_b = 180 \text{ kV/cm}$ 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 2/33/55/12), and measured a high W_{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_{rec} of 10.4 J/cm^3 and a η 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_{rec} and η 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_{rec} of $\sim 40 \text{ J/cm}^3$ while η only of $\sim 50\%$ 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_{rec} . In addition, note that antiferroelectric behavior can be observed at different formulas such as PLZT at $\text{Zr/Ti} \approx 52:48$ [196] or PLZST at $\text{Zr}/(\text{Sn}+\text{Ti}) \approx 65:55$ [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, $\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (PLZT 8/95/5) antiferroelectric ceramic films possess a high W_{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) NaNbO₃

NaNbO₃ (NN) is a well-documented nonpolar antiferroelectric phase and possesses a complicated crystal structure due to the rotation of oxygen octahedron

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

Composition	Category	<i>t</i>	$W_{\text{rec}} (\text{J/cm}^3)$	η (%)	ϵ_r @ RT	E_b (kV/cm)	Ref.
PZ	Thin film	300–600 nm	7.1	—	120–200	—	[164]
PSZ5	Thin film	500 nm	14.5	78	~150	900	[165]
$\alpha\text{-Fe}_2\text{O}_3$ modified PZ	Thin film	660 nm	17.4	~58	—	600	[169]
PZ:NiO	Thin film	140–170 nm	24.6	~70	~600	1000	[170]
Up-graded Eu-doped PZ	Thin film	400 nm	16.3	67.4	~300	1000	[168]
PLHS	Bulk	0.11 mm	7.63	94	~280	380	[176]
PHO	Thin film	330 nm	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 nm	40	53	—	1000	[194]
PLZT 8/95/5	Thick film	1 μm	53	—	~560	3500	[195]

PZ: PbZrO_3 ; PSZ5: $(\text{Pb}_{0.95}\text{Sr}_{0.05})\text{ZrO}_3$; PLHS: $\text{Pb}_{0.98}\text{La}_{0.02}(\text{Hf}_{0.45}\text{Sn}_{0.55})_{0.995}\text{O}_3$; PHO: PbHfO_3 ; PLZST 2/58/35/7: $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.58}\text{Sn}_{0.42}\text{Ti}_{0.02})\text{O}_3$; PBLZST: $(\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02})(\text{Zr}_{0.68}\text{Sn}_{0.24}\text{Ti}_{0.08})\text{O}_3$; PLZST 2/33/55/12: $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.33}\text{Sn}_{0.55}\text{Ti}_{0.12})\text{O}_3$; PLZS: $(\text{Pb}_{0.98}\text{La}_{0.02})(\text{Zr}_{0.55}\text{Sn}_{0.45})_{0.995}\text{O}_3$; PLSZS: $(\text{Pb}_{0.94}\text{La}_{0.02}\text{Sr}_{0.04})(\text{Zr}_{0.9}\text{Sn}_{0.1})_{0.995}\text{O}_3$; PLZT 2/95/5: $\text{Pb}_{0.98}\text{La}_{0.02}\text{Zr}_{0.95}\text{Ti}_{0.05}\text{O}_3$; PLZT 8/95/5: $(\text{Pb}_{0.92}\text{La}_{0.08})(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$.

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 $P_{\max}$ 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_{rec} . Moreover, Zhou *et al.* [208] firstly reported Bi_2O_3 modified NN energy storage ceramic bulks, obtained a high W_{rec} of 4.03 J/cm^3 for $\text{Na}_{0.7}\text{Bi}_{0.1}\text{NbO}_3$ ceramics at $E_b = 250 \text{ kV/cm}$ attributed to the disrupted random electric field and reduced domain size. Energy storage properties of $\text{Na}_{0.7}\text{Bi}_{0.1}\text{NbO}_3$ system show good temperature stability (20–100 °C), fatigue endurance (10^5 cycles), and charge–discharge properties. After that, more Bi-based compounds including $\text{Bi}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BMN) [209], $\text{Bi}(\text{Ni}_{1/2}\text{Sn}_{1/2})\text{O}_3$ (BNS) [210], and so on, are used to improve the relaxor characteristics and

acquire high W_{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 ST substrate exhibit antiferroelectric behavior, while that with (001) oriented substrate is still ferroelectric. Recently, Beppu *et al.* [212] obtained W_{rec} only of 2.9 J/cm^3 for 0.92NN–0.08SZ thin films at $E_b \approx 400 \text{ kV/cm}$. 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_{rec} and η of 1 mol% Mn thin films are 19.64 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 ($\sim 2.8 \text{ eV}$), 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_2O decomposition

Fig. 13 (a) Tolerance factor versus averaged electronegativity difference for $(\text{Na}_{1-x}\text{A}_{2+x})(\text{Nb}_{1-x}\text{B}_{4+x})\text{O}_3$ composition, where $(\text{A,B}) = (\text{Ca,Zr}), (\text{Ca,Hf}), (\text{Sr,Zr}),$ 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 $P_{\max}$ can up to $52 \mu\text{C}/\text{cm}^2$ at $220 \text{ kV}/\text{cm}$ 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_{rec} of $2.1 \text{ J}/\text{cm}^3$. In general, AN ceramics experience a series phase transition [218]:

where M1, M2, and M3 denote orthorhombic phases in rhombic orientation, O1 and O2 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 M1, M2, and M3. Therefore, reducing phase transition temperature among M1, M2, and M3 to low temperature would enhance W_{rec} of AN-based ceramics [218–221].

Chemical doping is a simple and effective method to enhance W_{rec} of AN-based ceramic bulks. For example, Ta^{5+} [218,222] and W^{3+} [223] substitute Nb^{5+} of B site, and Bi^{3+} [224], Ca^{2+} [225], and La^{3+} [226] replace Ag^+ of A site. In 2017, Zhao *et al.* [218] fabricated $\text{Ag}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ antiferroelectric ceramics, and P_r

decreases from 3.6 to $1.2 \mu\text{C}/\text{cm}^2$ whereas E_b enhances from 175 to $242 \text{ kV}/\text{cm}$ with increasing Ta content. $\text{Ag}(\text{Nb}_{0.85}\text{Ta}_{0.15})\text{O}_3$ exhibits a high W_{rec} of $4.2 \text{ J}/\text{cm}^3$, together with η of 69% , as shown in Figs. 14(a) and 14(b). The authors attribute the enhancement of W_{rec} to the low polarizability of Ta^{5+} because of a closed t value. Since then, Zhao *et al.* [223] have done some works to verify the possibility. Besides, electronegativity difference is also playing a crucial role in influencing the function behavior of antiferroelectric materials [227].

Note that fine-grain ceramics is a good choice 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 $E_b = 250 \text{ kV}/\text{cm}$ among pure AN ceramics so far. However, $P_{\max}$ has an obvious decrease compared with other AN ceramics using solid-state method, and thus W_{rec} and η are only of $1.8 \text{ J}/\text{cm}^3$ 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 , electronegativity 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 (a) P – E loops of AgNbO_3 and $\text{Ag}(\text{Nb}_{0.85}\text{Ta}_{0.15})\text{O}_3$ ceramic; (b) energy storage performances of $\text{Ag}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_3$ 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	<i>t</i>	W_{rec} (J/cm ³)	η (%)	ϵ_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 μ m	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 μ m	4.2	69	~200	233	[218]
AN	Bulk	150 μ m	~1.8	~40	~80	250	[228]

NN: NaNbO₃; SZ: SrZrO₃; CZ: CaZrO₃; AN: AgNbO₃; ANT15: Ag(Nb_{0.85}Ta_{0.15})O₃.

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 10² 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 ϵ_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 η , 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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