Progress In Lead Free- Relaxor Ferroelectrics For Energy Storage Applications.

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Abstract. The noticeable progression in the power electronic devices pushes a crucial demand to develop dielectrics with low loss, good temperature stability and high energy-storage density in addition to enhanced energy recovery characteristics. These properties are very important in order to use in advanced pulsed capacitors. Capacitors form a main part of many modern electrical and electronic devices. In this regards, relaxor ferroelectrics form an appropriate candidate for ceramic-based capacitor applications, due to their low loss and high energy density. This review provide theoretical basis at first, which help to evaluate the capacitors characteristics that contribute to high energy storage behavior. Moreover, serves to give an overall summary on latest development on electric energy-storage performance in the candidate materials, particularly in bismuth based peroviskite materials. For example, Bi\textsubscript{0.5}Na\textsubscript{0.5}TiO\textsubscript{3}, BiFeO\textsubscript{3} and their solid solutions with BaTiO\textsubscript{3} or with K\textsubscript{0.5}Na\textsubscript{0.5}NbO\textsubscript{3}.

Keywords: Energy storage density; Energy storage efficiency; Lead free ceramics; Ferroelectrics; relaxor ferroelectrics

1 Introduction

Climate change and the global air pollution in the last few decades created a global and strong desire to use clean renewable sources instead of the fossil fuel energy resources. Furthermore, develop new energy generation technologies such as wind, solar and thermal energy. As well as, fabricate new devices for effectively storing and supplying the electricity.

In regards of commercial energy storage devices, there are two classes based on the energy-storage time. The first used mainly for the long-term and stable energy supply and called long term, such as batteries, which are characterized by high energy-density about 10-300 W.h/kg, albeit their power density is quite low, typically lower than 500 W/kg, due to slow movement of the charge carriers. The second is named short term, such as capacitors, which are usually having high power density (10\textsuperscript{4}-10\textsuperscript{6} W/kg for electrochemical super capacitor and up to 10\textsuperscript{8} W/kg for dielectric capacitor). However, their energy density is small (typically below 30 W.h/kg). Therefore, they are usually used to generate a
pulsed voltage or current [1]. Figure 1 shows a diagram of the power density for different energy conversion and storage devices as a function of energy density [2].

![Figure 1](image.png)

**Figure 1** Power density as a function of energy density for different energy conversion and storage devices [2].

Nowadays, the traditional dielectric capacitors, that used commercially, are mainly made of dielectric (polymers or ceramics). These generally have an energy density of $10^{-2} - 10^{-1}$ W.h/kg (less than 2 J/cm$^3$) [3]. The most highly studied dielectric materials for energy storage can be divided into four categories: anti-ferroelectrics, polymer-based composites, glass-ceramics, and relaxor ferroelectrics [4]. Among these materials, relaxor ferroelectrics represent ideal candidates for energy storage applications such as capacitors, since they possess large maximum polarization, small remnant polarization and reasonable breakdown strength. Furthermore, significant improvements in recent years have been achieved in the energy storage density and reliability of these capacitors via a preparation of novel materials, diagnostic methods, and fabrication techniques [5]. This review aims to provide some physical principles of capacitors and energy storage measurements at first with highlighting the basic rules to explore the promising materials. Secondly, comprehensive information on research level of energy-storage in relaxors dielectric materials.

### 2 Fundamentals on dielectric capacitors.

Typically, a capacitor consist of two conductor parallel plates of area $A$ separated by a distance $d$, filled with certain dielectric materials, as shown in Figure 2. The function base of capacitors in the electronics devices is storing of electric energy. The ability of a capacitor to storage energy refers to as capacitance. Its value determined by geometry of the conductors and the relative permittivity of the dielectrics, as indicated in the following steps:
Firstly, the aforementioned parallel conductors joined to make simple electric circuit, as shown in Figure 3(a). Close this circuit causes giving a passing surge of current which rapidly decays to zero, as shown in Figure 3(b). As a result, charges (Q) are stored between capacitors plates which determine from integrate the area under the current (I) vs time (t) curve[6].

\[ Q = \int I \, dt \]  \hspace{1cm} (1)

\textbf{Figure 2} Schematic diagram of charge separation in parallel-plate capacitor under application of electric field [2].

\textbf{Figure 3} (a) Capacitor consist of parallel-plate of area A and separation d in vacuum attached to a voltage source. (b) Closing of the circuit causes a passing surge of current to flow through the circuit. Charge stored on the capacitor is equal to the area under the curve.

Applying different voltages V and plotting Q vs V results in a straight line relationship, as shown in Figure 4 and the following equation:

\[ Q = CV \]  \hspace{1cm} (2)

Where the C is the capacitance that obtained from the slope of Q-V curve, therefore the C₀ represent the capacitance of the parallel conductors in vacuum (free space), given by:
\[ C_{\text{vac}} = \varepsilon_0 \frac{A}{d} \quad (3) \]

where \( \varepsilon_0 \) is the permittivity of free space, which is a constant equal to \( \varepsilon_0 = 8.85 \times 10^{-12} \text{C}^2/(\text{J.m}) \). Farad (F) is the unit of capacitance, where \( 1 \text{ F} = 1 \text{ C/V} = 1 \text{ C}^2/\text{J} \) [6].

**Figure 4** Dependence of stored charge (Q) on applied voltage (V), slope of curve is associated to the dielectric constant of the material [6].

If a dielectric material is placed between the capacitor plates, Figure 5(a) and the aforementioned steps are repeated, the current that transmit through the external circuit and the storage charges on the capacitor plates will upsurge, as presented in Figure 5(b). Thus, it can be seen that applying different voltages and plotting the total charge stored on the capacitor versus the voltage applied will again result in a straight line but with a larger slope than that for vacuum, Figure 4. Therefore, Eq. (3) is now modified as follow:

\[ C = \varepsilon \frac{A}{d} \quad (4) \]

where \( \varepsilon \) is the permittivity of the material between the conductor plates.

The relative permittivity or dielectric constant of a material (\( \varepsilon_r \)) is defined as

\[ \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \quad (5) \]

Since \( \varepsilon \) is always greater than \( \varepsilon_0 \), the minimum value for \( \varepsilon_r \) is (1). By combining Eqs. (4) and (5), the capacitance of the metal plates separated by the dielectric is

\[ C = \varepsilon_r \varepsilon_0 \frac{A}{d} = \varepsilon_r C_{\text{vac}} \quad (6) \]

Thus \( \varepsilon_r \) is a dimensionless parameter that compares the charge-storing capacity of a material to that of vacuum.
The charge process will be finished when electrical potential caused by the stored charge ±Q on both plates is equal to the external applied voltage V. Q=V is equal to the capacitance C of the capacitor [7].

The alteration in polarization during the application of an electric field which represents charging and discharging polarization cycle can be represented graphically by P–E loop as shown in Figure 6. The behaviour of dielectrics upon this cycle represents a critical feature of energy storage dielectrics. This response can be used to estimate the stored energy, which should exclude hysteresis losses.

The following details help to better understand of the above process, where the Figure 6 depicts a slim hysteresis loop of a typical characteristic for the relaxor ferroelectric ceramics. There is a proportional relationship between polarization and electric field, where increasing of the electric field from zero to maximum electric field (E$_{\text{max}}$) over the charge process causes increases the polarization to the maximum P$_s$. Subsequently, the electric energy is stored in the dielectrics [8].

The value of electric energy W at E$_{\text{max}}$ level, that illustrated by the green and red area in Figure 6, was calculated by numeric integration of the P–E data based on the following equation [2]:

$$W = \int_0^{P_s} Ed\sigma, 0 \leq E \leq E_{\text{max}} \quad -----(7)$$

In contrast, upon decreasing of the electric field from E$_{\text{max}}$ to zero during the discharge process, the P$_s$ decreases to the P$_r$. Then, W$_{\text{rec}}$ (or W$_{\text{Stored}}$) is released on discharge from E$_{\text{max}}$ to zero. This demonstrated by the green area in Figure 6. Likewise, the W$_{\text{rec}}$ could be determined according to the equation below:
\[ W_{\text{rec}} = \int_{P_r}^{P_s} E \, dp \]  

(8)

On the other hand, the stored energy is not recovered completely, as demonstrated by the red area in Figure 6, due to the hysteresis loss. This part is called energy loss density \( W_{\text{loss}} \). On the other hand, the energy efficiency \( \eta \) can be calculated via following equation:

\[ \eta = \frac{W_{\text{rec}} - W_{\text{loss}}}{W_{\text{rec}}} \times 100\% \]  

(9)

**Figure 6** Mechanisms of electrical energy storage in relaxor ferroelectric ceramics[8].

Based on aforementioned analysis, to design ceramics with high \( W_{\text{rec}} \) for practical applications, they should be characterised by high dielectric breakdown strength (DBS) and large polarization difference \( (P_s - P_r) \) (i.e large \( P_s \), and small \( P_r \)).

Figure 7 shows representative P-E loops and an illustration of the energy-storage of four class of dielectric materials, namely: (a) linear dielectric (or paraelectric) with constant permittivity (e.g. \( \text{Al}_2\text{O}_3 \), glass), (b) antiferroelectric having zero net remnant polarisation \( (P_r) \) (e.g. \( \text{PbZrO}_3 \)), (c) ferroelectric with spontaneous polarisation (e.g. \( \text{PbTiO}_3 \), \( \text{BaTiO}_3 \)), and (d) relaxor ferroelectrics with nanosized domains, e.g. \( (\text{Pb,La})(\text{Zr,Ti})\text{O}_3 \) [2, 9, 10]. The hatched area in figure (yy) displays recoverable energy \( (W_{\text{rec}}) \), whereas the area enclosed by the hysteresis loop shows energy loss \( (W_{\text{loss}}) \).
Figure 7 Schematic description of the energy storage characteristics of (a) linear dielectrics, (b) antiferroelectrics, (c) ferroelectrics, and (d) relaxor ferroelectric ceramics [9].

3 Materials with energy storage performance.

3.1 Lead-based materials

Lead (Pb) based dielectric ceramic materials have been used extensively in energy storage applications due to processing high dielectric constant. Furthermore, they are exhibited various behaviour depending on temperature and compositional substitution, such as ferroelectric, antiferroelectric and relaxor ferroelectric[11]. In addition, lead based ceramics characterised by high Curie point ($T_c$) which permits a high temperature of operation (above 200 °C), can be easily poled, possess a wide range of dielectric constants, form solid solutions with many different constituents, thus allowing a wide range of achievable properties to meet the requirements of a specific application [12]. However, the environmental concerns have encouraged many researchers to focus on more environmentally friendly materials, since lead-based materials contain more than 60 wt.% of highly toxic lead oxide. Therefore, lead-free ceramics and films have been more widely studied compared to lead-based ceramics recently. Moreover, the lead-free materials have shown better energy storage performance than that of the lead-based materials[11].

3.2 Lead-free based materials.

3.2.1 BT based

Barium titanate, $BaTiO_3$ (BT) is developed in the mid of last century and represents one of the first piezoelectric materials, [13, 14]. This material exhibited a very high permittivity. Therefore, it consider as an excellent material for capacitors [15]. As mention above, the energy storage properties can be more enhanced by tuning the grain size. For instance, the grain size decreasing of the $BaTiO_3$ ceramic causes an increase of its relative permittivity, reaching $\varepsilon_r$ (max) of 5000 at grain sizes of about 0.8 to 1.1 μm [16, 17]. This is ascribed to stress effects and domain size. Moreover, the reduction in the grain size results in an increase in the dielectric breakdown strength (DBS) (which is also enhances the energy storage density) [18-21]. The DBS being about 8.5 kV mm$^{-1}$ when the grain size equal to
3.5 μm [22]. However, valuable lead-free materials are often produced after combination with other materials to form binary or ternary solid solutions.

Liu et al., investigated the effect of grain size on energy storage properties in BaTiO$_3$-based ferroelectric ceramics. They fabricate BaTiO$_3$ ceramics of different grain size doped with Al$_2$O$_3$-SiO$_2$ by two-step sintering. In addition, some samples were fabricated with extra dopant, namely ZnO as a sintering aid. It was found that the addition of ZnO results in an increase in the BDS and the density of ceramics without noticeable grain growth. Therefore, Al$_2$O$_3$-SiO$_2$-ZnO-doped samples with average grain size of $118\pm2$ nm results in an energy density of $0.83\pm0.04$ J/cm$^3$. In general, samples with fine grains have lower polarization but higher energy storage efficiency [23].

However, tailoring the energy storage properties by substitution doping at A- and/or B- sites (Ba$^{2+}$ and/or Ti$^{4+}$) in the perovskite structure of BaTiO$_3$ ceramic remain the effective approach to meet industrial application requirements [24].

A vital example of dopants that substitute Ba$^{2+}$ and Ti$^{4+}$ ions in BaTiO$_3$ ceramic are Ca$^{2+}$ and Zr$^{4+}$, respectively. The resulted ceramic is $(1-x)(BaZr_{0.2}Ti_{0.8}O_3)-(x)(Ba_{0.7}Ca_{0.3}TiO_3)$, which is denoted BCZT ceramic. This ceramic exhibited different properties based on the percentage of dopants, such piezoelectric, ferroelectric and energy storage properties. Puli et al [25] studied the ferroelectric dielectric, and energy density properties of this ceramic at $x=0.1, 0.15$ and $0.20$. The best properties were obtained in samples sintered at 1600 °C when $x=0.15$. Its permittivity was around 8400 and a low loss (tan$\delta$) of 0.014. Furthermore, they achieved an energy storage efficiency of about 70% as illustrated in Figure 8.

The same composition of the above BCZT ceramic was fabricated by the sol-gel rote by Wang et al [26], where an energy density of 0.52 J cm$^3$ was achieved. They ascribed it to the improved microstructure in comparison with that obtained by the conventional solid-state reaction method.

In recent years, many researchers investigated bismuth-based perovskite ceramics, symbolizes BiMeO$_3$, where Me denoted trivalent or averagely trivalent metallic ions, as a second member with Barium titanate in order to induce phase transformation to pseudo-cubic phase. Subsequently, relaxor ferroelectric behaviour can be obtained, which helps to improve the energy storage properties. These materials processes unique properties including a relatively high dielectric constant that remains stable over a wide temperature range [27-30] and high insulation resistance even at high temperature[31].
Shen et al [32] fabricated (1-x)BaTiO$_3$-xBiYbO$_3$ solid solutions successfully via conventional solid-state reaction method, with x = 0.00 ~ 0.20. The obtained ceramics exhibited tetragonal symmetry when x ≤ 0.05, and transform to pseudocubic at x ≥ 0.05 as illustrated in Figure 9 and Figure 10.

**Figure 9** (a), (c): XRD patterns for (1-x)BT-xBY ceramics; (b), (d): enlarged XRD patterns from 44.4° to 46.0° of (1-x)BT-xBY ceramics.

**Figure 10.** Lattice parameters for (1-x)BT-xBY ceramics as a function of BY content (x). Inset: the unit cell volume (V) as a function of composition.

P-E hysteresis loops measurements were employed to study the energy storage performance of the (1-x)BT-xBY ceramics. The results are illustrated in Figure 11. The obtained results reflects the findings that gained from the above XRD measurements. When x ≤ 0.05, the bulk ceramics were characterized as classic ferroelectrics, where typical hysteresis loops were obtained, as shown Figure 11(a).

As shown in Figure 11(a), the (1-x)BT-xBY bulk ceramics possess typical hysteresis loop as in classic ferroelectrics when x ≤ 0.05. Though, ceramics with x ≥ 0.06 were characterized by high polarization maxima (P$_s$) and low remanent polarization (P$_r$) exhibiting slim loops as presented in Figure 11(b), which reflect pseudocubic phase structure.
It is evident that $P_r$ and coercive field ($E_c$) were suppressed obviously, as displayed in the inset map at the right corner of Figure 11(b), that shows the developments of $P_r$ and $E_c$ as functions of the BY fraction. This is technologically important for energy storage, where a low $P_r$ and $E_c$ generally relate to low energy loss.

**Figure 11** P-E hysteresis loops of (1-x)BT-xBY ceramics, measured at room temperature; (a) $x \leq 0.05$ and (b) $x \geq 0.06$

The numerical integration was made at certain areas in the P-E loops in order to calculate the energy storage and loss densities ($W_1$ and $W_2$) or ($W_{\text{rec}}$ and $W_{\text{loss}}$), respectively, and consequently calculate the energy efficiency ($\eta$), as explained above using equation (8) and (9). Hence, the energy storage density and the energy efficiency should be both taken into account for practical applications. The obtained results are depicted in Figure 12. It was found that the energy loss density ($W_2$) of (1-x)BT-xBY ceramics decreased with increasing BY concentration, whereas the energy storage density ($W_1$) increases up to $x \sim 0.09$ then dropped.

In spite of remarkable enhancement in the energy efficiency with the increase of BY, the energy storage density does not improve due to low $P_r$, however, the highest energy storage density 0.71 J/cm$^3$ was obtained in ceramic with $x = 0.09$ at the electric field of 93 kV/cm.

**Figure 12** Calculated energy storage density ($W_1$ or $W_{\text{rec}}$), the energy loss density ($W_2$ or $W_{\text{loss}}$) and energy efficiency ($\eta$) of (1-x)BT-xBY ceramics as a function of BY content ($x$).
Many other of BaTiO$_3$–BiMeO$_3$ systems have been widely investigated lately, such as BaTiO$_3$–Bi(Zn$_{0.1}$Ti$_{0.5}$)O$_3$[27], BaTiO$_3$–BiAlO$_3$ [33–35], BaTiO$_3$–Bi(Mg$_{2/3}$Nb$_{1/3}$)O$_3$ [36, 37], BaTiO$_3$–Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$ [32, 38]. However, all these studies focused on energy storage properties at room temperature and dielectric properties at elevated temperature. In contrast, few workers were concerned in energy storage properties in a wide temperature range. Though, it is very important characteristic for electric power systems operating suitably in a wide temperature range. For example, the power systems in hybrid electric vehicles operates in temperature range of -40 °C to 140 °C [39, 40]. Moreover, good temperature stability of the capacitors make them work properly without need for assist cooling systems in this temperature range.

Recently, Chen et al, [41] were studied the (1-x)BaTiO$_3$-xBi(Zn$_{0.5}$Zr$_{0.5}$)O$_3$ ((1-x)BT–xBZZ) solid solution in terms of the phase composition, dielectric properties and ferroelectric properties. They found that the phase structure is gradually transform from a tetragonal phase to a pseudocubic phase, with an increasing BZZ content, in the range 0.01 ≤ x ≤ 0.3. This causes a transition from ferroelectric-like behavior to a diffusive and dispersive relaxor-like characteristic.

Among this range of compositions, Yuan et al [31], investigated the energy storage properties of the 0.9BaTiO$_3$–0.1Bi(Zn$_{0.5}$Zr$_{0.5}$)O$_3$ solid solution, via studying structural and ferroelectric characteristic upon heating, focusing on the temperature stability. Unipolar P–E loops for that ceramic were measured during heating in a temperature range of 30–150 °C at 10 Hz and at 200 kV cm$^{-1}$, as shown in Figure 13(b). It is evident that the temperature has a great influence on P–E loop shape. Upon heating, the P$_i$ decreases slowly and the P$_t$ slightly increases, which results in a small difference between them varying slightly from 22.1 µC cm$^{-2}$ to 17.7 µC cm$^{-2}$. This variation in temperature-dependent polarization is attributed to the diffusive phase transition in wide-ranging, which is the characteristic feature of relaxor ceramics.

This stable variation in polarization under 200 kV cm$^{-1}$ causes change in the energy density from1.35 J cm$^{-3}$ to 1.72 J cm$^{-3}$, as well as a high value range of the energy efficiency of 81.7–86.8%, as presented in Figure 13(c). These findings showed that there is a small variation over a wide measured temperature range, which indicate that the 0.9BT–0.1BZZ ceramic have outstanding temperature stability for high energy storage applications.

In addition, the energy density of the 0.9BT–0.1BZZ ceramics exhibited proportional relationship with applied electric field at different temperatures up to their breakdown strength, as shown in Figure 13(d). The energy densities of the 0.9 BT–0.1BZZ ceramics at 30 °C, 60 °C, 90 °C, 120 °C and 150 °C, are 2.46 J cm$^{-3}$, 2.21 J cm$^{-3}$, 1.83 J cm$^{-3}$, 1.62 J cm$^{-3}$ and 1.39 J cm$^{-3}$, respectively. The highest value of the energy density was 2.46 J cm$^{-3}$, which was observed at ambient temperature and at the electric field of 264 kV cm$^{-1}$.
Figure 13 Fig. 7 (a) Schematic unipolar P–E loop, shows of the energy storage properties for dielectrics (b) P–E loops of the 0.9BT–0.1BZZ ceramics measured over a temperature range of 30–150 °C at 10 Hz and at 200 kV cm\(^{-1}\). (c) Energy density and efficiency at 200 kV cm\(^{-1}\) as functions of temperature from 30 °C to 150 °C. (d) Dependence of energy density on electric field for the 0.9BT–0.1BZZ ceramics at different temperatures.

Lately, the \((1-x)\text{BaTiO}_3-x\text{Bi(Zn}_{1/2}\text{Zr}_{1/2})\text{O}_3\) ferroelectric ceramic was studied also by Wang et al, in composition range \(0 \leq x \leq 0.20\) \([42]\). A high \(W_{\text{rec}}\) of 2.47 J/cm\(^3\) and a large \(\eta\) of 94.4\% are simultaneously realized in relaxor ceramic composition of BT-12BZZ by means of increase the BDS value as a result of reduced grain size and low dielectric loss. Figure 14 illustrates bipolar and unipolar P-E loops that used to measured \(W_{\text{rec}}\) and \(\eta\), likewise the procedure that done above, by Yuan\([31]\).
Figure 14 (a) Bipolar and (b) unipolar P-E hysteresis loops at a frequency of 1 Hz and under a driven electric field of 120 kV/cm, (c) corresponding $P_{\text{max}}$, $P_{\text{r}}$, $P$ derived from bipolar P-E loops as a function of BZZ fraction and (d) calculated $W_{\text{rec}}$, $W$, and $\eta$ derived from unipolar P-E loops of BT-BZZ ($0.00 \leq x \leq 0.20$).

3.2.2 BNT based materials

This material was reported for the first time in the 1960s by Smolenskii et al. Albeit it did not attract attention until 1990s because there was no definitive structural understanding. Moreover, it is characterized by some drawbacks such as high coercive field, high conductivity and low depolarization temperature ($T_d$) around 187 °C, which is lower than its Curie temperature 325 °C. This drawback limits use it at elevated temperatures. Thereafter, some of the initial dielectric and optical property measurements of NBT reported in several studies [43]. In addition, many methods were adopted by scientist to address the main issues. Hiruma et al. found that the addition of excess bismuth results in an increase in the resistivity, consequently overcome the problem of high conductivity that was ascribed to volatilization of Bi ions during sintering [44]. For the lower depolarization, the literature attributes that to the existence of an intermediate antiferroelectric phase [45, 46, 47], albeit other works claim that the intermediate phase is not fully antiferroelectric [44]. However, the NBT materials is a promising material due to its high Curie temperature of 325 °C, and a piezoelectric constant of 73 pC/N, which similar to that of BT [29].

In recent years, different dopants were used in different studies to develop new properties of NBT materials and to overcome the aforementioned drawbacks at the same time [35-38 ref Aksel 2010]. [47]

In terms of the doping sites, it is worth noting that NBT consist of complex ions on the A-site, where has a mixture of Bi$^{3+}$ and Na$^+$ ions. As a result, substitution is more effective on the A-site. Unlike PZT materials where B-site is active due to the existence of complexity ions on the B-site (Ti$^{4+}$ and Zr$^{4+}$) [48].
In regards of energy density properties, Zhao et al. [49] studied the effect of B-site \((\text{Al}_{0.5}\text{Nb}_{0.5})^{4+}\) complex-ion substitution on the structural and ferroelectric characteristics, in addition to the energy storage properties of \((\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{Ti}_{1-x}(\text{Al}_{0.5}\text{Nb}_{0.5})_x\text{O}_3\) (BNBT-xAN) ceramics. Doping with AN resulted in slimmer P–E loops (i.e. large difference between the \(P_s\) and \(P_r\)) as shown in Figure 15. This can be attributed to phase transformation from ferroelectric phase to the mixture of ferroelectric and antiferroelectric phase in the BNBT-xAN ceramics, consequently change to relaxor ferroelectric phase [50]. This behavior is similar to the results in the \((1-x-y)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3-y\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3\) piezoelectric ceramics [51]. Thus high energy storage density can be gained, where at the composition of \(x=0.04\) and electric field of 70kV/cm, the energy storage density reached the optimum value of 0.70 J/cm\(^3\) and the corresponding energy storage efficiency is 60\%. as can be seen in Figure 16.

![Figure 15 P–E hysteresis loops of the BNBT-xAN ceramics](image)

On the other hand, the energy storage efficiency increases with the increase of the AN fraction, where the largest energy storage efficiency of 76\% is obtained at \(x=0.07\), as illustrated in Figure 16.

![Figure 16 Compositional dependence of energy storage density (W) and energy storage efficiency (\(\eta\)) of the BNBT-xAN ceramics](image)
Other efforts were made to produce BNT based ceramics having stable energy storage properties. This feature consider as an urgent demand nowadays due to the rapid development of numerous emerging applications. It is well known that induce production of phase coexistence material by doping is the most successful way for tailoring stable dielectric and energy storage properties. Zhu et al. [52] designed a new system by modifying 0.95Bi0.5Na0.5TiO3–0.05SrZrO3 (BNTSZ) ceramics with NaNbO3 (NN) ((1-x)BNTSZ–xNN) to attain the coexistence of rhombohedral and tetragonal phases. This kind of phase coexistence in BNT based materials resulted in favorable stable energy storage properties. The produced ceramics exhibited a large discharge energy density of 3.14 J cm⁻³ at x=0.15 with an energy efficiency of 79% at a high temperature of 120 °C under 230 kV cm⁻¹. The variation in the discharge energy density being less than ±4% in the temperature range from 25 °C to 180 °C under 120 kV cm⁻¹, which indicate a stable energy storage performance. Figure 17 showed the development of dielectric and ferroelectric properties with increasing of NN fraction. P–E hysteresis loops change from an anti-ferroelectric to a nearly linear like shape with increasing of NN fraction, as can be seen in Figure 17(b).

![Figure 17](image)

**Figure 17** (a) Temperature-dependent dielectric permittivity and loss of the (1-x)BNTSZ–xNN ceramics; NN fraction varying from 0.05 to 0.2 (b) P–E loops, measured under an electric field of 160 kV cm⁻¹ at 1 Hz.

### 3.2.3 BF based materials

In recent years, pure Bismuth ferrite, BiFeO₃ (BF), material attracted researcher’s attention among the Bi-based ferroelectric ceramics for many reasons. It processes multiferroic nature at room temperature [ref 4 ilkan 2018] and exhibited interesting phase transition up on heating. For example, an antiferromagnetic-paramagnetic phase transition at around 370°C and ferroelectric-paraelectric at Curie point at around 825 °C that represents another feature for this ceramic which enable it to use in high temperature application. However, still there are many drawbacks prevent it to usage as a pure form. For instance; high leakage current, low piezoelectric coefficients and hard to produce at elevated temperatures due to the volatility of bismuth oxide which causes formation of second phases. In addition, hard to poled due to the high coercive field [53-56].

However, the issues that related to the production are solved through using various processing methods [57-60]. On the other hand, partial substitutions at A– and B– site ions in the perovskite structure of BiFeO₃, was employed to enhance its characteristics properties [61-69].

Formation of solid solution with barium titanate BiFeO₃–BaTiO₃ (BF–BT) attracted particular attention lately. It had been intensively studied as promising candidates due to their potential applications at high temperature.
In regards of optimisation the energy storage density, Ilkan et al. [70] investigated 0.75BiFeO$_3$-0.25BaTiO$_3$ (75BFBT) ceramics doped with 1 mol% La. They found that the microstructure development is dependent strongly on the way of dopants incorporation. Their results exhibited that doping with isovalent substitution yielding relatively homogeneous large-grained structures. On the other hand, they found that donor substitution leading to the formation of fine-grained core-shell type morphology.

For donor-substituted ceramics, they noticed relaxor ferroelectric character in LaBa ceramics, where the ferroelectric switching behaviour was constrained relatively, as shown in Figure 18. The dielectric energy storage density of resulted ceramic was 0.61 J cm$^{-3}$ at an electric field of 10 kV mm$^{-1}$. This high value can be ascribed to the presence of the core-shell type grain with the evidence of pseudocubic phase in the shell, which reduces dielectric nonlinearity and hysteresis. This can be explain a follow; the ferroelectric domain switching in the ferroelectric core regions is constrained by the ergodic relaxor ferroelectric nature in the shell regions, within which the polar nanoregions are unable to form long range-ordered ferroelectric domains under the influence of the electric field.

This way to improve the energy storage density (i.e by induce formation of core-shell type microstructures) has been also experimentally described in BaTiO$_3$-BiScO$_3$ and BaTiO$_3$-SrTiO$_3$ [71, 72]. It was also suggested that the control of the shell phase volume play an important role for optimising energy storage density [73].

![Figure 18](image-url) (a) P-E hysteresis loops for LaBa ceramics with various maximum electric field levels and (b) quadrant of the P–E loop with the illustration of stored energy density, $W_{\text{Stored}}$ and energy loss, $W_{\text{Loss}}$.

### 3.2.4 KNN based materials

The solid solution system, potassium niobate–sodium niobate, KNbO$_3$–NaNbO$_3$ (alternatively (K, Na)NbO$_3$ or KNN) is another lead-free perovskite material that possess valuable ferroelectric properties. Both end members of the solid solution crystallises as an orthorhombic perovskite at room temperature[74]. The formula K$_{0.5}$Na$_{0.5}$NbO$_3$ is the most popular composition due to its nearness to the morphotropic phase boundary (MPB) which occurs at about 52.5% Na [37K]. However, it is difficult to produce KNN ceramics with high sintered density because its production should achieved low sintering temperatures due to the instability of the KNN phase above 1140 °C and volatility of the alkali species at high temperatures [75, 76].
In order to improve the energy storage properties of KNN ceramics, many workers tried to reduce the grain size using certain additives. Their efforts had shown promising results. Qu et al [40] fabricated KNN ceramic have an energy storage density of 2.48 J cm\(^{-3}\) and a dielectric breakdown strength (DBS) of 29.5 kV mm\(^{-1}\) through reducing the grain size to 0.5 μm through the addition of Sr(Sc\(_{0.5}\)Nb\(_{0.5}\))O\(_3\) (SSN), albeit they reported the presence of porosity at the grain boundaries. Furthermore, the addition of 0.5 mol% ZnO results in high dense KNN-SNN samples, which leads to achieve a breakdown strength of 40 kV mm\(^{-1}\) and an energy storage density of 2.6 J cm\(^{-3}\) [77].

Shao et al, [8] investigated inducing high \(W_{	ext{rec}}\) of \((\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\)-Bi(\(M_{\text{2/3}}\text{Me}_{1/3}\))O\(_3\) (where \(M^{2+}=\text{Mg}^{2+}\) and \(\text{Zn}^{2+}\)) by means of increase DBS and \(P_s\), hence the \(W_{	ext{rec}}\) of bulk ceramics is critically limited by these parameters. In terms of the influence of adding Bi-based materials on the structure and ferroelectric properties of pure KNN, they reported that the crystal structure is changed gradually from a orthorhombic (for pure KNN ceramics) to a pseudocubic for \(x (\text{BMN content})\) of 0.05 and 0.10, then to cubic phase for \(x=0.15\) and \(x=0.2\) due to the disappearance of splitting of the (202) / (020) peak, as shown in Figure 19.

![Figure 19 XRD patterns of (1-x)KNN-xBMN ceramics](image)

XRD results are correlated with the measured P-E loops that illustrated in Figure 20. It was evident that pure KNN ceramics exhibit normal ferroelectric behaviour represented by square P-E loops with large \(P_r\), which is not favourable for high \(W_{	ext{rec}}\) because of large hysteresis loss. However, the ferroelectric switching behaviour was changed with addition of BMN, where the P-E hysteresis loops of (1- \(x\))KNN-xBMN ceramics transform gradually to slim loops for \(x >0.10\). Almost linear P-E relationships can be observed for 0.8KNN-0.2BMN ceramics. These results indicate that the ferroelectric properties of (1-x)KNN-xBMN ceramics are dramatically decreased with the increase of BMN fraction. \(P_s\) and \(P_r\) can be seen to decrease significantly with increasing BMN content. For example, the \(P_s\) and \(P_r\) values are 51, 41, 18, 4 μC/cm\(^2\) and 23, 8, 4.5, 0 μC/cm\(^2\) for (1-x)KNN-xBMN ceramics with \(x = 0.05, 0.10, 0.15\) and 0.20, respectively.
Figure 20 P–E hysteresis loops of (1-x)KNN-xBMN ceramics.

Therefore, we can understand that they proposed two strategies to increase the $W_{\text{rec}}$ of lead-free ceramics. The first is compositions dominate the grain size of lead-free ceramics to submicron scale to increase the DBS and the second is the hybridization between the Bi 6p and O 2p orbits enhances the $P_s$. They achieved large $P_s$ (41 $\mu$C/cm$^2$) and high DBS (300 kV/cm) in 0.90KNN-0.10BMN ceramics, which leading to large $W_{\text{rec}}$ of 4.08 J/cm$^3$, as shown in Figure 21.

![Graph showing P–E hysteresis loops](image)

**Figure 21** Total and recover energy storage densities of (1-x)KNN-xBMN ceramics.

Yang et al [78] follow the strategy which state that the decreasing of grain size improve the DBS and subsequently led to enhance the energy storage properties. In this matter, they studied reduction the
grain size of KNN materials to submicrometer via compositional substitution by SrTiO$_3$. (1-x)(K$_{0.5}$Na$_{0.5}$)NbO$_3$-xSrTiO$_3$ ceramics. As can be seen in Figure 22, it is evident that they succeed in preparation of (1-x)KNN-xST ceramics at x=0.15 and 0.20, with the submicrometer grain sizes of ~0.3μm using conventional solid state method.

Figure 22 Grain size distributions of (1-x)KNN-xST ceramics.

In order to calculate the energy storage density and its efficiency, they measured the P-E loops of (1-x)KNN-xST ceramics at certain electric fields as presented in Figure 23. Evidently, the saturated or square loop for pure KNN ceramics transform gradually to a slim loop with the addition of SrTiO$_3$. This denoted that the ferroelectric switching behavior of (1-x)KNN-xST ceramics are reduced dramatically with increasing of ST content. This can be ascribed to non-ferroelectricity behavior of SrTiO$_3$ at room temperature. Furthermore, the increase of ST content caused changing in the symmetry from orthorhombic for pure KNN (x=0) to the pseudocubic phase or cubic phase for x=0.15.
and 0.2, i.e induce formation of relaxor ferroelectrics. This is obviously shown from slim hysteresis loops, which are another typical characteristic for the relaxor ferroelectrics behavior.

**Figure 23** P-E hysteresis loops of (1-x)KNN-xST ceramics.

Figure 24 depict energy storage properties of (1-x)KNN-xST ceramics with x=0.15 and 0.2 at the varied electric fields. The largest $W_{rec}$ of 4.03 J cm$^{-3}$ was obtained in 0.85KNN-0.15ST ceramics at DBS of 400 kV cm$^{-1}$ with the thickness of 0.2mm. This value is superior to all other $W_{rec}$ in lead-free bulk ceramics. On the other hand, the 0.80KNN-0.20ST ceramics exhibited large $W_{rec}$ of 3.67 J cm$^{-3}$ and energy storage efficiency of 72.1%.

**Figure 24 (a) and (b)** The calculated energy storage density $W$ and the recoverable energy storage density $W_{rec}$ from P-E loops of ceramics with x= 0.15 and 0.2, respectively.

### 4 Summery

In summary, we reviewed briefly the study on high energy-storage relaxor dielectrics over the past few years. A number of material systems have been explored in terms of their energy storage properties. Most of them focused on modifying the difference between the maximum polarization and the remnant polarization. Furthermore, improve higher electric breakdown field to optimize the energy storage performance to meet practice requirements. Some possible ways were proposed to achieve this goal (enhance the energy-storage behavior). The most important one represented by substitutional doping, which employed to tailor the coexistence of phases or to induce transition to pseudocubic phase (which is the characteristic feature of relaxor ferroelectrics). Furthermore, to causes grain...
growth inhibitions which help to reduction the grain size, consequently, improve dielectric breakdown strength. However, still there are unlimited and more complicated solid solutions and doping strategies can be followed to enhance the energy storage density. Overall, the aforementioned studies reveal that the relaxor ferroelectrics are a promising candidate for the electrical energy storage application.

5 References

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