Flexible lead-free BFO-based dielectric capacitor with large energy density, superior thermal stability, and reliable bending endurance

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Abstract
As an essential energy-stored device, the inorganic dielectric film capacitor plays an irreplaceable role in high-energy pulse power technology area. In this work, propelled by the challenge of overcoming the bottlenecks of inflexibility and inferior energy storage density of the pure BiFeO₃ films, the mica with high bendability and thermal stability is adopted as substrate, and the relaxor ferroelectric [(Sr₀.7Bi₀.2)TiO₃]BO₂ (BFMO-SBT) thin film capacitor exhibits a high recoverable energy storage density (W_{rec} = 61 J cm⁻³) and a high efficiency (η = 75%) combined with a fast discharging rate (23.5 μs) due to the large polarization difference (ΔP = 59.4 μC cm⁻²), high breakdown strength (E_B = 3000 kV cm⁻¹), and the strong relaxor dispersion (γ = 1.78). Of particular importance is the capacitor presents excellent stability of energy storage performance, including a wide working temperature window of -50-200 °C, fatigue endurance of 10⁸ cycles, and frequency range of 500 Hz-20 kHz. Furthermore, there are no obviously deteriorations on energy storage capability under various bending states and after 10⁸ times of mechanical bending cycles. All these results indicate that BFMO-SBT on mica film capacitor has potential application in the future flexible electronics.

1. Introduction
Energy consumption is ever-increasing in the world due to the fast growth of the population and the economy, which will inevitably lead to the running out of fossil fuel resources and accompanied air pollution and global warming. In order to solve the problem, great efforts have been put worldwide into the exploita-
tion and utilization of renewable and clean energy resources, e.g., solar and wind. In the view of the intermittency of these energies, it is of utmost indispensability to develop energy storage systems, which can store energy temporarily or for a long time. Compared with the long-term energy storage device (such as batteries) [1–3], the electrostatic capacitors possess the advantages of fast energy uptake and delivery and long cycling life, and thus hold a great potential to be used in high power-energy-storage applications [4,5], such as hybrid electrical vehicles, electrical weapon systems, and microwave communications [6].

In the current era of “Internet-of-Things”, flexible electronics have sparked active research efforts due to the potential application in the next-generation smart electronic devices [7,8]. Compared with the traditional rigid-based electronics, flexible counterparts are portable, light-weight, foldable, stretchable and even wearable [9]. Among the current commercial dielectric materials, ceramics have some typical common features of high stiffness and excellent thermal stability, in contrast to extraordinary flexibility and limited working temperature of the polymers [4,10,11]. Therefore, there is an increasingly urgent demand for the high-performance energy storage capacitor with superior thermal stability and reliable

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bending endurance.

Recently, the appearance of MICtronics, revealing that the transparent Mica can be a promising universal flexible supporter for deposition of oxide functional films, breaks a new path to develop flexible electronics. Inorganic Mica is referred to as one of well-known stacked-layered silicate compounds, in which there exists strong intralayer interaction but weak interlayer van der Waals force. It can be easily to prepare a thin sheet of mica with good flexibility, cyclability and transparency via mechanical exfoliation using tweezers or sticky tape like the separation of graphite [12,13]. Artificial fluorophlogopite mica (FMica) possesses substantial unique features like atomically flat surface, elasticity, light-weight, and chemical inertness such as antioxidant ability and acid/alkali-resistance, and so on [9]. Specially, the desired thermal stability (>950 °C) makes it compatible with the crystallization temperature for inorganic dielectric film [14,15]. Researches about all-inorganic flexible energy-storage capacitors are carried out successively recently. Shen et al. reported that the PLZT thick film fabricated on LaNiO3/F-Mica substrate, which has a high recoverable energy-storage density (Wrec of 40.2 J cm−3) and the energy efficiency (η) of 81%, together with excellent stability of energy-storage performance under mechanical bending cycles of 2000 times [16] and Bisay et al. found that flexible Ba(Zr0.5Ti0.5)O3 films exhibit ultrahigh energy storage performances (Wrec=65.1 J cm−3 and η=72.8%) as well as excellent mechanical flexibility (104 times of mechanical bending cycles) and ferroelectric fatigue endurance (106 charging-discharging cycles) [17]. Recently we have designed flexible Na0.5Bi0.5TiO3-based films capacitors with giant and stable energy storage performances [18,19]. For example, the flexible 0.55(0.94Na0.5Bi0.5TiO3-0.06BaTiO3)-0.45SrTiO3 film capacitor shows a desirable Wrec of 76.1 J cm−3 and a high η of 80.0% due to the predominant relaxor feature and weak antiferroelectric-like behavior [19].

Noticeably, perovskite BiFeO3 (BFO) has been demonstrated as a ferroelectric relaxor candidate. Pure BFO has ultrahigh Curie temperature (Tc~830 °C) [20], indicating the possibility to work in harsh operating temperature. However, the strong ferroelectric performance with a robust theoretical remanent polarization (Pr~100 µC cm−2) made it unsuitable as energy storage material [21]. Very recently, Nan and Lin group has successfully achieved BFO-based solid-solution films with ultrahigh-energy density via polymorphic nanodomain design (e.g., Wrec = 112 J cm−3 and η = 80% for BFO-BT-ST; Wrec = 70 J cm−3 and η = 70% for BFO-ST) [22,23]. Nevertheless, these reports on BFO-based films are all synthesized on rigid substrates such as single-crystalline Nb:STO. Despite excellent performance obtained in BFO-based dielectric capacitors without mechanical bending capability, the flexible alternatives are highly desirable in consideration of the advent of flexible electronics technology.

In this work, we propose to utilize the relaxor feature of another dielectric composition to form solid solution with BFO to reduce remanent polarization while maintain large saturation polarization. 5 mol% Mn2+ substituted BFO with low leakage current is selected as the base system. (Sr1-xBi1-x)TiO3 with high Bi concentration of x = 0.2, which provides ferroelectric-relaxor behavior with diffused dielectric maxima in the temperature range of 10–200 K, is used as a second component to form a solid solution with composition of 0.3Bi(Fex0.05Mnx0.95)2O3-0.7 Sr0.5Bi0.5TiO3 (BFMO-SBT). The BFMO-SBT thin film was directly deposited on mica substrate via simple one-step fabrication process. A high Wrec of 61 J cm−3, together with a large η of 75% are concurrently achieved in BFMO-SBT film capacitor. Besides, the excellent energy storage capability remains stable within a wide working temperature window of −50–200 °C, even after experiencing fatigue endurance of 108 cycles and in a frequency range of 500 Hz–20 kHz. Notably, the flexible BFMO-SBT film capacitor exhibits prominent mechanical-bending resistance without obvious deterioration in energy storage performance.

2. Material and methods

2.1. Film fabrication

A mica substrate with smooth, clean mica surface was obtained from a fluorophlogopite mica [KMg3[AlSi3O10]F2] (Changchun Taiyuan Fluoranthene Co., Ltd., Changchun) via a simple mechanical exfoliation process. A bottom electrode with a 30 nm-thick Pt layer was sputtered onto the mica surface. BFMO-SBT thin film was deposited on mica substrates via a chemical solution coating processing. For the preparation of the BFMO-SBT precursor sol gel, designed stoichiometric ratios of manganese acetate tetrahydrate, bismuth acetate, pentahydrate, iron nitrate nonahydrate, strontium acetate, and tetrabutyl titanate were used as raw materials, in which 5 mol% excess Bi was added to compensate for the Bi volatilization during annealing treatment at high temperature. In addition, acetylacetone was added to the mixed solution as a stabilizing agent, and 2-methoxypentanol and acetic acid were used as the solvents. The final concentration of the precursor solution was 0.3 M. After aging for 24 h, the solution was spin-coated on the Pt mica substrate in an ambient atmosphere with a rotation speed of 3000 rpm for 30 s and then the wet thin film was baked at 250 °C on a hot plate for 2 min. Each wet film was subsequently pyrolyzed at 350 °C for 5 min and then annealed at 580 °C for 10 min in a rapid thermal processor. The processes of spin coating and heat treatment were repeated until a desired thickness was achieved. In order to construct a capacitor structure for electrical measurements, Pt point electrodes with a radius of 100 µm were sputtered on the film using a custom-designed shadow mask. To realize the flexibility, the obtained film capacitor was peeled off with very thin mica layer from the thick mica using tweezers and scotch tapes.

2.2. Characterization

An X-ray diffractometer (XRD) with Cu Kα radiation (XRD, Bruker D8) was used to identify the phase structure of the sample. The surface morphology of the film was detected by atomic force microscopy (AFM, Bruker dimension icon). The cross-sectional microstructure was characterized by a field-emission scanning electron microscope (FESEM, Hitachi S-4200). The polarization-electric field (P–E) loops, and insulating characteristic were measured using a standard ferroelectric tester (Precision Pro, Radiant Technologies). An impedance analyzer (HP4294A) was used to measure the dielectric properties. The temperature-related electrical tests were carried out with the aid of a temperature-controlled probe station (Linkam-HFS600E-PB2). The local domain pattern was carried out on the film with driving voltage applied at the tip using piezoresponse force microscope (PFM). The fast discharge test was performed by a homemade resistance-capacitance (RC) circuit with a load resistance of 100 kΩ.

3. Results and discussion

A number of BFMO-SBT thin films were fabricated on Pt/mica substrates under the same experimental conditions. After peeling off the bottom mica layer by layer, the mica can be thinned down to several micrometers to realize high flexibility, as shown in Fig. 1a. After being bended, the film surface has no obviously mechanical damages of cracks, shrinkages, and exfoliation, which is the basic premise for preparing flexible energy storage capacitor. The flexible BFMO-SBT/Pt/mica heterostructure under flat and bending states are illustrated in Fig. 1b and c.
The x-ray diffraction pattern of BFMO-SBT grown on Pt/mica substrate was scanned with a speed of 2° min⁻¹ from 20° to 60°. As shown in Fig. 1d, after subtracting the Pt and mica diffraction peaks, the rest of detectable diffraction peaks confirm the film are fully crystallized as a pure polycrystalline perovskite structure without detectable secondary phases. The surface AFM image of BFMO-SBT film was scanned over an area of 2 × 2 μm², as shown in Fig. 1e. A relatively dense microstructure can be obtained without cracks. And the average surface roughness (R_a) is only 2.05 nm, suggesting that the surface is flat. Distinct interface at the interfaces of BFMO-SBT/Pt and Pt/mica can be observed in Fig. 1f. The thickness of BFMO-SBT thin film is measured as 300 nm. Also, there are no obvious large voids found in the fracture surface, which will reduce leakage to some extent.

Fig. 2a shows the dielectric behaviors containing ε_r and tanδ as functions of temperature ranging from -50 to 300 °C. Typical dielectric relaxation signatures, represented by the frequency dispersion of ε_r and a broad peak of maximum ε_r, are observed in the temperature range of 150–280 °C. The relaxor dispersion degree around the dielectric peak can be analyzed using the modified Curie-Weiss equation of 1/ε_r-1/ε_m=(T-T_m)/C, where T_m and ε_m are the temperature of the dielectric peak and the maximum ε_r at T = T_m, respectively, C is a Curie constant and γ represents the diffuseness degree. The relationship of ln(1/ε_r-1/ε_m) and ln(T-T_m) and the fitting is shown in Fig. 2b. The value of γ is 1.78, which further demonstrates the strong relax behaviour of BFMO-SBT. This result is consistent with NBT-SBT multilayer ceramics, where a certain amount of SBT as a modifier can enhance the dielectric relaxation behavior [10]. For tanδ, its values are less than 0.5 for both the frequency range from 100 Hz to 1 MHz and temperature range from -50 to 300 °C. The low tanδ loss will inhibit the performance deterioration which could be caused by the thermal runaway and self-heating. Fig. 2c shows the ε_r and tanδ as functions of frequency for BFMO-SBT. From 100 Hz to 100 kHz, the ε_r shows a slightly decrease due to the insufficient dipoles mobility [24], while the tanδ shows imperceptible change with the frequency increasing. At 100 kHz, ε_r and tanδ for the BFMO-SBT thin film is 377 and 0.05, respectively.

To further verify the relaxor characteristic in BFMO-SBT film, the domain dynamics is investigated by means of piezoresponse force microscope (PFM). Fig. 2d is the PFM phase images of the BFMO-SBT film before and after poling treatment with relaxation durations of 0 min, 10 min and 20 min, respectively. For pure BFO film, previous report has demonstrated that its polarization can be maintained at least 10 h after poling treatment [23]. A striking contrast is observed in this work, namely, almost imperceptible signal feedback emerges in the corresponding electrically excited regions and this phenomenon becomes more and more serious after long-term relaxation of 30 min. The result proves a highly dynamic response of the microscopic ferroelectric domain to external electric field in BFMO-SBT film. In other word, the switched domains in the film can quickly recover to its original state when remove the external stimuli due to the presence of highly-dynamic polar nano-regions. This is in accordance with the small macroscopic remanent polarization reflected in the P-E loop.

It is necessary to confirm the dielectric breakdown electric field strength E_b since a large E_b is highly desirable in order to realize a high W_rec [25]. The value of E_b can be evaluated by Weibull analysis:

\[ X_i = \ln(E_i) \] (1)

\[ Y_i = \ln(-\ln(1 - i / (n + 1))) \] (2)

where E_i is the E_b of the specimen, i (i = 1, 2, 3 …) is the serial number of the sample, n is the sum of specimens for a sample. E_i is arranged in a gradual increase tendency as follows.

\[ E_1 < E_2, \cdots < E_i, \cdots < E_n \] (3)

Fig. 2e depicts Weibull distribution of E_b for the BFMO-SBT film. The solid fitting straight line is the result of Weibull analysis for ten data collected from our film sample. The slope parameter \( \beta \), represented the scattering property of all measured E_b data, is 9.52, which indicates both the good composition uniformity and high dielectric reliability for BFMO-SBT film. The average E_b extracted by the horizontal intercept is about 3011 kV cm⁻¹, which is much larger than that of BFMO thin film reported in our previous work [26].

The P-E loops for BFMO-SBT film were measured at 10 kHz and 25 °C, up to 3000 kV cm⁻¹ which is slightly lower than E_b, as shown...
in the insert of Fig. 2e. The corresponding variations of \( P \) are summarized in Fig. S1. From these \( P-E \) loops, the \( W_{\text{rec}} \) and \( \eta \) can be calculated according to the following equations:

\[
W_{\text{rec}} = \frac{P_{\text{max}}}{P_r} EdP \tag{4}
\]

\[
\eta = \frac{W_{\text{rec}}}{W} \times 100\% = \frac{W_{\text{rec}}}{W_{\text{rec}} + W_{\text{loss}}} \times 100\% \tag{5}
\]

where \( E \) is the electric field, \( P, P_r \) and \( P_{\text{max}} \) are the polarization, remanent polarization and maximum polarization, respectively. \( W \) presents the whole stored energy density during the charging process, \( W_{\text{loss}} \) stands for the energy loss density. The \( W, W_{\text{rec}}, W_{\text{loss}} \) and \( \eta \) at various electric fields were calculated based on \( P-E \) loops and shown in Fig. 2f. It can be found that with the \( E \) increasing, the \( W_{\text{rec}} \) and \( W \) show the increscent tendencies due to the enhanced polarization while the \( \eta \) decreases due to the fact that \( W_{\text{loss}} \) increases faster than \( W_{\text{rec}} \). As a result, a high \( W_{\text{rec}} \) of 61 J cm\(^{-3}\) together with a big \( \eta \) of 75% can be realized at the large electric field of 3000 kV cm\(^{-1}\). Simultaneously, the discharging characteristic was evaluated using an external resistor of 100 k\( \Omega \), as shown in Fig. 2g. It is seen that the BFMO-SBT film liberates a relatively high density of 34.73 J cm\(^{-3}\) under 2000 kV cm\(^{-1}\) electric field. And the time required for discharging 90% of the stored energy is about 23.5 ms, which is comparable to the discharge speed of \( \text{Ba(Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3/\text{Ba(Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3 \) film on Nb:STO substrate (41.4 ms) [27].

It is well known that good thermal stability, high fatigue endurance and wide working frequency are highly desirable for practical applications of energy storage dielectric capacitors. Fig. 3a presents the \( P-E \) hysteresis loops of BFMO-SBT film as a function of temperature and the corresponding temperature evolution of \( W_{\text{rec}} \) and \( \eta \) is summarized in Fig. 3b. It is revealed that the pinched \( P-E \) loops have not evolved into a square shape when the temperature increases from \(-50 \) to 200 \( ^{\circ} \)C, with the values of \( P_m \) only increasing from 52 to 55 \( \mu \)C cm\(^{-2}\), while \( P_r \) maintained at around 2 \( \mu \)C cm\(^{-2}\) (Fig. S2). The corresponding temperature dependent \( W_{\text{rec}} \) and \( \eta \) are not obvious with slightly fluctuation in the wide temperature range (\( W_{\text{rec}} \sim 38 \) J cm\(^{-3}\), \( \eta \sim 82\%)\), indicating an excellent thermal stability of the BFMO-SBT capacitor. The outstanding thermal stability in the
wide temperature window (-50-200 °C) will endow the capacitors working under harsh environment, for instance, using in the fields of hybrid electric vehicles (-140 °C), drilling operations (150–200 °C) as well as solar and wind inverter at high altitudes or in polar regions (-90 °C) [28–32]. The minor variation with temperature may be attributed to slight increase of the electrical conduction with rising of temperature, which is reflected in the J-E curves under different temperature (Fig. S3). The tiny increase of leakage current can be explained by the enhanced ionic conductivity stemmed from thermal activation process.

Next, the fatigue behavior of the film is evaluated, which is implemented with fast charging-discharging cycles at 2000 kV cm⁻¹ and 10 kHz. As presented in Fig. 3c, no significant degradation is found in the P-E loops after 10⁸ cycles, which is further confirmed by the summarized \( P_m \) and \( P_l \) values evolution (shown in Fig. S4). The changes of \( W_{rec} \) and \( \eta \) during fatigue are illustrated in Fig. 3d and the degradations of \( W_{rec} \) and \( \eta \) after 10⁸ cycles are both within 5%, manifesting high fatigue endurance capability of the BFMO-SBT film capacitor. The excellent fatigue endurance behavior can be attributed to the reduction of oxygen vacancy concentration by introducing Mn ions and the highly dynamic nano-scale domain switching [33]. The rapid nano-domain response to the external electric field has been proven in Fig. 2d. Finally, the frequency reliability is examined as shown in Fig. 3e and f, corresponding to the frequency response of the P-E loops and the critical energy storage parameters, respectively. The change of
polarization in a fairly large frequency range of 0.5–20 kHz is very small (Fig. S5), that is $W_{\text{rec}}$ keeps around 38 J cm$^{-3}$ while $\eta$ slightly increases with increasing the frequency, suggesting a high frequency stability. Such weak dependence on frequency indicates only a small contribution of the leakage current, nonlinear dielectric effects, and fast switching of domains [15]. In view of the above results, the obtained stable energy storage performances in such broad temperature, cycling times and frequency ranges are superior than the previous reported BFO-based film [33].

In order to investigate the energy storage properties of the flexible BFMO-SBT film against mechanical bending, electrical measurements were carried out under two kinds of bending states, namely compressive state and tensile state with various radii (from 12 mm to 2 mm). The bending test is realized by attaching the film on different molds, which possess downward and upward curved surfaces as shown in the inset of Fig. 4a and b. The ferroelectric P-E loops with almost the same shape were obtained when the film is only bent to the radii from 12 to 2 mm as shown in Fig. 4a and b. To make more explicit description of the variation of the P-E loops under different bending states, the $P_m$ and $P_r$ values extracted from the P-E loops are shown in Fig. S5 in which no obvious changes are observed, indicating remarkable mechanical bending endurance of the flexible capacitor. Moreover, only 2% degradation of $W_{\text{rec}}$ and $\eta$ in all the bending test is observed, as shown in Fig. 4c. This shows that the compressive/tensile strain has minor influence on the energy storage performance. The excellent bending resistance ability makes our capacitor capable to be used in harsh mechanical conditions, showing great potential in the field of flexible devices. Fig. 4d and e shows the discharging characteristics of the film in the compressive and tensile states under various bending radii at 2000 kHz, respectively. The corresponding time-discharged voltage relationships are shown in Fig. S7. Clearly, no obvious variation of the energy density and discharge rate can be found under different compressive and tensile states, demonstrating it has the capability to quick-release the stored energy both in upward and downward bending conditions. The result is even more apparent in the discharged energy density/discharge speed-bending radius curves, as shown in Fig. 4f. These encouraging results show that the BFMO-SBT based capacitor has great potentials as flexible embedded capacitor to be integrated in electronic devices.

Then, the fatigue endurance under the two bending states and the mechanical bending endurance by exerting $10^4$ bending cycles were validated, respectively. As shown in Fig. 5a and b, even after $10^4$ fatigue switching cycles, the $W_{\text{rec}}$ and $\eta$ are able to keep at high values of ~36 J cm$^{-3}$ and ~82%, regardless of the stress states and the bending radius (even as low as 4 mm). The insets are the P-E curves before and after $10^5$ switching cycles, which corresponds to the downward and upward bending states, respectively. All loops maintain slim shapes without obvious deterioration in $P_m$ and $P_r$ after the fatigue test (Fig. S8). Fig. 5c and d sums up the P-E loops and corresponding energy storage performance after $10^3$ times of repeated mechanical bend tests. It is found that the ferroelectric P-E loops remain minor changed even after $10^5$ times of bending cycles. The stable values of $W_{\text{rec}}$ and $\eta$ further prove that the energy storage performance of the capacitor with excellent mechanical bending endurance. The changes of $P_m$ and $P_r$ have a similar tendency as $W_{\text{rec}}$ and $\eta$ (Fig. S9). These results confirm that the BFO-based flexible capacitor has wide application foreground for implementing energy storage capabilities in flexible electronics.

Table 1 summarizes the typical properties of several representative dielectric films on rigid or flexible substrates. The energy storage performance and working temperature range of BFMO-SBT film on mica in this work are superior than the reported Pb$_{0.92}$La$_{0.12}$Zr$_{0.05}$Ti$_{0.95}$O$_3$ [36] and can rival other lead-free dielectric films on rigid substrates [34,35,37]. But the obtained energy storage density ($W_{\text{rec}}$=61 J cm$^{-3}$) is inferior to the monoclinic films of 0.6BiFeO$_3$-0.45SrTiO$_3$ ($W_{\text{rec}}$=70.3 J cm$^{-3}$) and (Na$_{0.5}$Bi$_{0.5}$)$_{0.9118}$La$_{0.02}$Ba$_{0.0052}$Ti$_{0.97}$Zr$_{0.03}$O$_3$ ($W_{\text{rec}}$=154 J cm$^{-3}$) fabricated on SrTiO$_3$ single crystals [23,38]. However, the high temperature tolerance in BFMO-
SBT exceeds all other representative ferroelectric films on rigid substrates. Note that the film also displays a good balance between $W_{rec}$ and $\eta$ when compared with the antiferroelectric films of $\text{Pb}_{0.96}\text{La}_{0.04}\text{Zr}_{0.98}\text{Ti}_{0.02}\text{O}_3$ and $\text{Pb}_{0.97}\text{Y}_{0.02}\{\text{Zr}_{0.6}\text{Sn}_{0.4}\}_{0.925}\text{Ti}_{0.075}\text{O}_3$ on rigid Si substrates [39,40]. Additionally, the excellent antifatigue feature of the BFMO-SBT ($1/\text{C}^{108}$) outperforms most of the listed inorganic films, which can satisfy the application requirement. Meanwhile, compared with the reported flexible films on mica, the obtained energy storage density in this work is obviously improved except for $\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$ film on LSMO/STO/Mica substrate [17] and NBT-based ternary system on Pt/mica substrate [18]. It is noted that the bending radius of 2 mm is much smaller than that in flexible $\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$ ($R = 4$ mm) and $\text{Pb}_{0.93}\text{La}_{0.09}$ ($Z_{0.05}\text{Ti}_{0.35}\text{O}_{0.975}\text{O}_3$ ($R = 5$ mm) films [16,17,41]. And the bending resistance ($10^4$) ability in this work is almost as good as the other flexible ferroelectric elements. All these results suggest that the flexible BFMO-SBT capacitor meet the actual requirements of the flexible energy storage devices.

4. Conclusions

In summary, excellent energy-storage performance with a high

### Table 1
Comparison of energy storage performance of our BFMO-SBT film with other different materials on rigid or flexible substrates.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Substrates</th>
<th>$E$ (kV cm$^{-1}$)</th>
<th>$W$ (J cm$^{-3}$)</th>
<th>$\eta$ (%)</th>
<th>Temperature range (°C)</th>
<th>Fatigue Minimum radius (mm)</th>
<th>Bending cycles</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid</td>
<td>$0.6\text{BiFeO}_3-0.4\text{SrTiO}_3$</td>
<td>SrTiO$_3$ single crystal</td>
<td>3850</td>
<td>70.3</td>
<td>70</td>
<td>50-100</td>
<td>$10^3$</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>$\text{Bi}<em>{1.25}\text{La}</em>{0.75}\text{Ti}<em>3\text{O}</em>{12}/\text{BiFeO}<em>3/\text{Bi}</em>{1.25}\text{La}_{0.75}\text{Ti}<em>3\text{O}</em>{12}$</td>
<td>Pt/Ti/SiO$_2$/Si</td>
<td>2753</td>
<td>65.5</td>
<td>74.2</td>
<td>30-140</td>
<td>$10^3$</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>$\text{Ba}_2\text{Bi}<em>4\text{O}</em>{11}$</td>
<td>Pt/Ti/SiO$_2$/Si</td>
<td>2340</td>
<td>37.1</td>
<td>91.5</td>
<td>100-180</td>
<td>$2 \times 10^3$</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>$\text{Pb}<em>{0.9}\text{La}</em>{0.1}\text{Zr}<em>{0.925}\text{Ti}</em>{0.075}\text{O}_3$</td>
<td>$\text{LaNiO}_3$</td>
<td>2141</td>
<td>38</td>
<td>71</td>
<td>20-150</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>$0.7\text{Na}_0.2\text{Bi}_0.3\text{Ti}_0.7\text{O}_3$</td>
<td>Pt/Ti/SiO$_2$/Si</td>
<td>2612</td>
<td>60</td>
<td>51</td>
<td>20-180</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>$0.4\text{Na}_0.2\text{Bi}_0.3\text{Ti}_0.7\text{O}_3$</td>
<td>$\text{La}_0.7\text{Sr}_0.3\text{MnO}_3/\text{SrTiO}_3$</td>
<td>3500</td>
<td>154</td>
<td>97</td>
<td>30-110</td>
<td>$10^3$</td>
<td>--</td>
</tr>
<tr>
<td>Flexible</td>
<td>$\text{BaZr}<em>{0.35}\text{Ti}</em>{0.65}\text{O}_3$</td>
<td>ITO/Mica</td>
<td>4230</td>
<td>40.6</td>
<td>48.9</td>
<td>120-150</td>
<td>$10^3$</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\text{BaZr}<em>{0.35}\text{Ti}</em>{0.65}\text{O}_3$</td>
<td>LSMO/STO/Mica</td>
<td>6150</td>
<td>69.4</td>
<td>84.7</td>
<td>100-200</td>
<td>$10^4$</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\text{Pb}<em>{0.9}\text{La}</em>{0.1}\text{Zr}<em>{0.925}\text{Ti}</em>{0.075}\text{O}_3$</td>
<td>$\text{LaNiO}_3$/Mica</td>
<td>1998</td>
<td>40.2</td>
<td>61</td>
<td>30-180</td>
<td>$10^3$</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>$0.97(0.93\text{Na}_0.2\text{Bi}_0.3\text{Ti}_0.7\text{O}_3-0.07\text{BaTiO}_3)/0.03\text{BiFeO}_3$</td>
<td>Pt/Mica</td>
<td>2285</td>
<td>81.9</td>
<td>64.4</td>
<td>200-200</td>
<td>$10^3$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>$0.3\text{BiFeO}<em>3-0.7\text{Sr}</em>{0.2}\text{Bi}_0.2\text{Ti}_0.8\text{O}_3$</td>
<td>Pt/Mica</td>
<td>3000</td>
<td>61.5</td>
<td>75.4</td>
<td>50-200</td>
<td>$10^3$</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 5. (a) and (b) are the ferroelectric fatigue endurance of the BFMO-SBT capacitor measured in a compressive and tensile state with a bending radius of 4 mm, respectively. (c) and (d) are the change of $W_{rec}$ and $\eta$ of the capacitor during $10^4$ cycles of mechanical bend with radius of 4 mm, respectively. The insets are the P-E curves under initial state and after fatigue or repetitive bending cycles measurement.
W_{ac} of 61 J cm\(^{-2}\) and a big η of 75% together with an ultrafast discharge rate of 23.5 μs has been achieved in the all-inorganic flexible BFMO-SBT thin film capacitor. The energy storage behavior maintains well under different measuring conditions such as changing temperature from −50 to 200 °C, experiencing 10\(^8\) reduplicative charge-discharge cycles, and varying frequency in the range of 500 Hz-20 kHz. Also, the flexible BFMO-SBT film capacitor exhibits strong mechanical-bending resistance under various bending states and repetitive bending cycles. The combination of these attractive characteristics endows the BFMO-SBT thin film capacitor for the practical application in flexible microenergy-storage systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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