

Efficiently enhanced energy storage performance of $Ba_2B_4Ti_5O_{18}$ film by co-doping Fe^{3+} and Ta^{5+} ion with larger radius

Qiong Wu(吴琼), Lei Zhao(赵雷), Xinghao Chen(陈兴豪), and Shifeng Zhao(赵世峰)

Citation: Chin. Phys. B, 2022, 31 (**9**): 097701. DOI: 10.1088/1674-1056/ac5393
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Epitaxially strained $SnTiO_3$ at finite temperatures

Dawei Wang(王大威), Laijun Liu(刘来君), Jia Liu(刘佳), Nan Zhang(张楠), Xiaoyong Wei(魏晓勇)
Chin. Phys. B, 2018, 27 (**12**): 127702. DOI: 10.1088/1674-1056/27/12/127702

Effect of an electric field on the electrocaloric response of ferroelectrics

Hongbo Liu(刘宏波)
Chin. Phys. B, 2018, 27 (**12**): 127701. DOI: 10.1088/1674-1056/27/12/127701

Electrical analysis of inter-growth structured $Bi_4Ti_3O_{12}$–$Na_{0.5}Bi_{4.5}Ti_4O_{15}$ ceramics

Xiangping Jiang(江向平), Yalin Jiang(江亚林), Xingan Jiang(江兴安), Chao Chen(陈超), Na Tu(涂娜), Yunjing Chen(陈云婧)
Chin. Phys. B, 2017, 26 (**7**): 077701. DOI: 10.1088/1674-1056/26/7/077701

Hysteresis loop behaviors of ferroelectric thin films: A Monte Carlo simulation study

C. M. Bedoya-Hincapié, H. H. Ortiz-Álvarez, E. Restrepo-Parra, J. J. Olaya-Flórez, J. E. Alfonso
Chin. Phys. B, 2015, 24 (**11**): 117701. DOI: 10.1088/1674-1056/24/11/117701

Magnetic and ferroelectric properties of Zn and Mn co-doped $BaTiO_3$

Sangram Keshari Das, Binod Kumar Roul
Chin. Phys. B, 2015, 24 (**6**): 067702. DOI: 10.1088/1674-1056/24/6/067702

Efficiently enhanced energy storage performance of $Ba_2Bi_4Ti_5O_{18}$ film by co-doping Fe^{3+} and Ta^{5+} ion with larger radius

Qiong Wu(吴琼), Lei Zhao(赵雷), Xinghao Chen(陈兴豪), and Shifeng Zhao(赵世峰)†

Inner Mongolia Key Laboratory of Nanoscience and Nanotechnology, & School of Physical Science and Technology, Inner Mongolia University, Hohhot 010021, *China*

(Received 26 November 2021; revised manuscript received 17 January 2022; accepted manuscript online 10 February 2022)

We present an efficient strategy, that is the co-substitution of Fe^{3+} and Ta^{5+} ions with large radius for Ti^{4+} ion, to enhance energy storage performance of $Ba_2Bi_4Ti_5O_{18}$ film. For the films co-doped with Fe^{3+} and Ta^{5+} ions, the maximum polarization under the same external electric field is improved because the radius of Fe^{3+} and Ta^{5+} ions is larger than that of Ti^{4+} ion. Moreover, due to the composition and chemical disorder, the relaxor properties are also slightly improved, which can not be achieved by the film doped with Fe^{3+} ions only. What is more, for the films doped with Fe^{3+} ion only, the leakage current density increases greatly due to the charge imbalance, resulting in a significant decrease in breakdown strength. It is worth mentioning that the breakdown strength of Fe^{3+} and Ta^{5+} ions co-doped film does not decrease due to the charge balance. Another important point is the recoverable energy storage density of the films co-doped with Fe^{3+} and Ta^{5+} ions has been greatly improved based on the fact that the maximum external electric field does not decrease and the maximum polarization under the same external electric field increases. On top of that, the hysteresis of the polarization has also been improved. Finally, the co-doped films with Fe^{3+} and Ta^{5+} ions have good frequency and temperature stability.

Keywords: $Ba_2Bi_4Ti_5O_{18}$ film, ferroelectrics, energy storage, co-doped, radius

PACS: 77.80.–e, 68.55.–a, 84.60.Ve **DOI:** 10.1088/1674-1056/ac5393

1. Introduction

Electric dipoles within ferroelectrics can respond to external electrical stimuli, which allows ferroelectrics to store electrical energy.[1–4] When an electric field is applied through the two measured electrodes, the ferroelectric film capacitors are charged. After removing the external electric field, the stored electric energy is released in the scale of milliseconds.[5,6] For practical applications, ferroelectric film capacitors are always expected to have high energy density, efficiency, power density, excellent frequency stability, temperature stability and so on.[7] However, for most ferroelectrics, they are not suitable for energy storage because of their low polarizability, breakdown strength and high dielectric loss. So far, the energy density released by ferroelectric film system in a charge–discharge process has been improved to more than 150 J/cm^3.[8]

Many innovative approaches have been proposed to improve energy storage performance. In terms of the final effect, these approaches can be basically divided into two categories. According to the formula for the recoverable energy density $W_{\rm rec} = \int_{P_{\rm r}}^{P_{\rm m}} E\,{\rm d}P$, where $P_{\rm r}$ and $P_{\rm m}$ are the remnant and maximum polarizations of ferroelectric film under the external electric field E, it can be seen that high external electric field and large difference between $P_{\rm m}$ and $P_{\rm r}$ can obtain large recoverable energy density.[9] Therefore, the first strategy is to improve the breakdown strength so that ferroelectric film capacitors can operate in a high external electric field. The second strategy is to improve the polarizability of ferroelectric films so that they can achieve higher polarization under the same external electric field. Meanwhile, the remnant polarization should be reduced as much as possible. For the former, there are many ways to increase the breakdown strength. For example, Pan *et al*. introduced paraelectric $SrTiO_3$ in conventional ferroelectric $BiFeO_3$ to transform macroscopic electric domains into highly-dynamic polar nano-regions.[10] As the content of $SrTiO_3$ gradually increased from 30% to 75%, the maximum external electric field ($E_{\rm m}$) increased from 2750 kV/cm to 4460 kV/cm. And energy storage performance had also been greatly improved. However, the $P_{\rm m}$ under the same external electric field (1500 kV/cm) gradually decreases as the proportion of $SrTiO_3$ increases. The $P_{\rm m}$ decreases by nearly 20 μC/cm^2 as the proportion of $SrTiO_3$ increases from 30% to 75%. This decrease is significant, especially for the fact that the $P_{\rm m}$ of the $0.7BiFeO_3$–$0.3SrTiO_3$ film is just over 40 μC/cm^2 under external electric field of 1500 kV/cm. Finally, the discharged energy density of the $0.25BiFeO_3$–$0.75SrTiO_3$ film (70 J/cm^3) is lower than that of the $0.4BiFeO_3$–$0.6SrTiO_3$ film (70.3 J/cm^3), although the maximum external electric field of the former (4460 kV/cm) is higher than that of the latter (3850 kV/cm). In conclusion, the high breakdown strength of paraelectric $SrTiO_3$ has a positive contribution to the energy storage performance of the system, while the ultra-low polarization has a negative effect. What is more, Zhang *et al*. select $PbZr_{0.52}Ti_{0.48}O_3$ and linear dielectric Al_2O_3 to form composite film with sandwich structure.[11]

†Corresponding author. E-mail: zhsf@imu.edu.cn

© 2022 Chinese Physical Society and IOP Publishing Ltd

Although the maximum electric field of the composite film reaches 5711 kV/cm, the P_m is still less than 30 μC/cm^2. In practical application, such a high external electric field can easily lead to the occurrence of electrode injection behavior, which increases the probability of thermal breakdown.[12,13] And it is also increases the probability of danger. If the film operates at a relatively low external electric field, such low polarization is not conducive to a good energy storage performance. For the second type, ferroelectrics with large lattice distortion, such as $BiFeO_3$, are usually introduced into the original system in order to obtain higher polarization.[14–17] Song *et al.* prepared $(1-x)Bi_{0.2}Sr_{0.7}TiO_3$–$xBiFeO_3$ films, and the results showed that as the proportion of $BiFeO_3$ increases, the maximum polarization under the same external electric field (2000 kV/cm) increased by about 30 μC/cm^2.[18] However, $BiFeO_3$, as a typical conventional ferroelectric, can promote the transformation of the original domains into macroscopic domains. This leads to a significant reduction in efficiency. Therefore, the increase in discharged energy density is very low, and the increase is less than 10 J/cm^3 at an external electric field of 2000 kV/cm.

According to the current research status and practical application requirements of ferroelectric film capacitor, it should have a suitable and moderate working electric field (2000 kV/cm–4000 kV/cm), an appropriate P_m (50 μC/cm^2–150 μC/cm^2) in the range of working electric field, so as to ensure that it is possible to obtain an ideal energy storage density, and finally, a high efficiency ($> 80\%$). Ignoring the improvement of polarization in pursuit of very high working electric field is not conducive to the comprehensive improvement of energy storage performance. Similarly, it is not satisfactory to ignore the improvement of efficiency in order to pursue high polarization. Based on this, $Ba_2Bi_4Ti_5O_{18}$ (BBT) was selected as the object. BBT is a typical relaxor ferroelectric with the Aurivillius structure consisting of oxygen octahedral (perovskite-like) blocks interleaved with $(Bi_2O_2)^{2+}$ layers.[19] The strong relaxor properties of BBT are thought to be due to the random electric fields created by the compositional and chemical disorder of the A-site cations, which is beneficial to induce a weak polarization hysteresis behavior.[19] What is more, the $(Bi_2O_2)^{2+}$ layer has the effect of inhibiting the diffusion of space charges and defects.[20] This gives BBT unparalleled fatigue resistance. These features make BBT a candidate for energy storage applications. Previous studies have shown that BBT film has high efficiency, moderate operating electric field, but low P_m.[21,22] This makes the energy storage density of BBT films low. At present, the highest energy storage density of BBT film is 41.2 J/cm^3 with the efficiency of 79.1%.[23] According to previous studies, the replacement of Ti^{4+} by ions with larger radius, such as Fe^{3+}, will produce tensile chemical stress, which reduces free energy and improves polarization.[18,20] Based on this, a series of $Ba_2Bi_4Ti_{5-x}Fe_xO_{18}$ films were prepared with $x = 0$, 0.03, 0.06, 0.09, 0.12 (dubbed as BBT, F3, F6, F9, F12). As the content of Fe^{3+} increases, P_m under same external electric field are greatly improved, but efficiency and breakdown strength are gradually reduced. And then, a series of $Ba_2Bi_4Ti_{5-x}(Fe_{0.5}Ta_{0.5})_xO_{18}$ films were prepared with same x value (dubbed as BBT, FT3, FT6, FT9, FT12). The radius of Ta^{5+} and Fe^{3+} are both larger than that of Ti^{4+}, which helps to maintain a high polarization. The charge balance is realized by introducing Ta^{5+} and Fe^{3+} together, so that the breakdown strength does not decrease. What is more, The introduced Fe^{3+} and Ta^{5+} also induce compositional and chemical disorders in the BBT films. This helps to improve the relaxor properties of BBT films. So that efficiency is not decreased, but slightly improved. Finally, the energy storage performance of all co-doped films have been all-side improved. This results show that Ta^{5+} and Fe^{3+} with larger radius together replace Ti^{4+} is an effective way to improve energy storage performance of BBT film.

2. Experimental details

2.1. Fabrication of films

All the processes of preparation of sol were performed at room temperature. The solvents mentioned below were mixtures of glycol and glycol methyl ether with a volume ratio of one to one. For $Ba_2Bi_4Ti_{5-x}Fe_xO_{18}$ sols, $(CH_3COO)_2Ba$, $Bi(NO_3)_3{\cdot}5H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were added to a beaker sequentially. The weight of $Bi(NO_3)_3{\cdot}5H_2O$ required an excess of 10% to compensate for its volatilization during annealing process. After all solutes are completely dissolved, $C_{16}H_{36}O_4Ti$ was slowly dropped into the beaker. Then, by adding solvent, the concentration of the solutions was adjusted to 0.03 mol/L. For $Ba_2Bi_4Ti_{5-x}(Fe_{0.5}Ta_{0.5})_xO_{18}$ sols, the previous steps are the same. In addition, quickly dropped $C_{10}H_{25}O_5Ta$ into another beaker containing 5 ml acetic acid. After the substances in the two beakers were completely dissolved, they were mixed together. The concentration of the solutions was adjusted to 0.03 mol/L by adding solvents. After the sols had aged for 120 h, it could be crystallized on the Pt(111)/Ti/SiO_2/Si substrate. First, the sol was dropped on the substrate holding for 15 s at 500 r/min and then for 35 s at 7000 r/min. Then the films were dried at 320 °C for 3 min and crystallized at 725 °C for 3 min using rapid thermal annealing system. The steps above were repeated until the films reached a certain thickness and finally annealing at 725 °C for 15 min.

2.2. Characterization

X-ray diffraction (XRD, Kratos Amicus, UK) with Cu *K*a radiation was used for structural characterization. Scanning electron microscopy (SEM, Hitachi SU4800) was used to

measure the thickness of films. The *P*–*E* hysteresis loops and leakage properties of the film were characterized by multiferroic tester system (Multi Ferroric, RT, USA). And temperature control system (Instec mK2000) was used to achieve temperature changes.

3. Results and discussion

The thickness of BBT film is about 200 nm (Fig. S2(a)). For all doped films, their thicknesses are also considered to be 200 nm due to the very low doping amount. Figure 1(a) shows the *P*–*E* hysteresis loops of $Ba_2Bi_4Ti_{5-x}Fe_xO_{18}$ films under external electric field of 1000 kV/cm. It can be seen that BBT film has a very slim shape of *P*–*E* hysteresis loop due to its strong relaxor properties, which contributes to a high energy storage efficiency.[20] Nevertheless, a high energy storage density cannot be obtained because of very low polarization. With the gradual increase of Fe^{3+} content, there is a significant increase in P_m (Fig. 1(c)). They are 27.5, 44.3, 48.9, 58.3, and 70.9 μC/cm^2 respectively. The P_m of F12 film is 2.5 times higher than that of BBT film. Such a huge increase is due to the fact that the radius of Fe^{3+} (0.609 Å) ion is larger than that of Ti^{4+} (0.569 Å) ion, which can create tensile chemical pressure in the lattice.[24] This tensile chemical pressure reduces the fourth and sixth Landau coefficients α_{11} and α_{111} in the Landau energy density ($f_{\text{Land}} = \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6 - EP$) and further increase polarization.[20,25,26] However, the introduction of Fe^{3+} ions can not only enhance the polarization, but also stabilize the long-range ferroelectric order.[27] This is conducive to the formation of macro domains and increase P_r. And eventually, the shape of the *P*–*E* hysteresis loops change significantly. The P_r of F-series films are 2.3, 5.3, 7.5, 10.7, and 18.1 μC/cm^2 respectively. The P_r of F12 is almost eight times that of BBT. These changes increase energy loss during charge-discharge process, which is detrimental to energy storage performance.

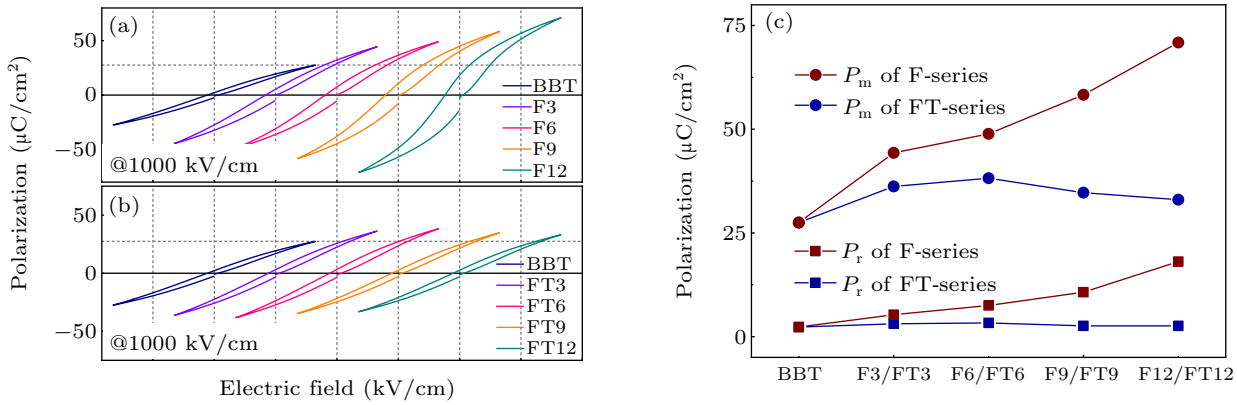


Fig. 1. The *P*–*E* hysteresis loops under the external electric field of 1000 kV/cm of (a) F-series and (b) FT-series films with the same scale of ordinates. (c) P_r and P_m (1000 kV/cm) of F-series and FT-series.

Then, Ta^{5+} ions are further introduced into the system in order to achieve compositional and chemical disorders, which contributes to the enhancement of relaxor properties and *P*–*E* hysteresis loop with a slender shape.[19,20] The radius of Ta^{5+} (0.69 Å) ion is also larger than that of Ti^{4+} (0.569 Å) ion.[24] This is also conducive to the improvement of polarization. As shown in Fig. 1(b), all *P*–*E* hysteresis loops in the FT-series films have a nearly slender shape. The P_r of FT-series films are 2.3, 3.1, 3.3, 2.6, and 2.6 μC/cm^2 respectively. This is a very small change, especially compared with the corresponding F-series films. More than that, the P_m of Ta^{5+} and Fe^{3+} co-doped films still has a improvement compared with BBT films. They are 27.5, 36.2, 38.2, 34.7, and 33 μC/cm^2 respectively. The P_m of FT6 film is the largest, and then the P_m decreases slightly with the increase of Ta^{5+} and Fe^{3+} content. This is because a small amount of impurity phase appears in the FT9 and FT12 films. As shown in Fig. 2(a), all diffraction peaks of BBT film are correspond very well to standard PDF cards 01-073-6259 from the International Centre for Diffraction Data. The sharp (10$\underline{1}$1) and (10$\underline{1}$7) diffraction peaks indicate that all the films have good crystallization state. When the content of (FeTa) increases to 0.09, a new small peak appears at the position of $2\theta = 34.78°$, which belongs to the (221) diffraction peak of $Bi_2Fe_4O_9$ (04-009-3974). And $Bi_2Fe_4O_9$ has very low dielectric constant and very weak ferroelectricity.[28,29] This causes a small drop in the polarization of the system. This is consistent with the position changes of diffraction peaks (10$\underline{1}$1) and (10$\underline{1}$7) (Figs. 2(b) and 2(c)). According to Bragg's law, when Ti^{4+} ions are replaced by Fe^{3+} and Ta^{5+} ions with large radius, the diffraction peaks will move to a lower theta. (10$\underline{1}$1) and (10$\underline{1}$7) peaks gradually move to the left when the content of (FeTa) is lower than 0.09. As the content of (FeTa) continues to increase, the two diffraction peaks have no obvious movement, which is caused by the formation of impurity phase.

The *I*–*E* loops of F-series and FT-series films under external electric field of 1000 kV/cm are shown in Fig. S1. For BBT films, a typical relaxor ferroelectric, the current peaks

caused by domain switching are very diffuse. With the increase of Fe^{3+} content, current peaks gradually become sharp and move to both ends. This shows that the relaxor properties of the system decreases significantly. And the films tend to conventional ferroelectrics. This is because Fe^{3+} ion stabilizes the long-range ferroelectric order. For films co-doped with Fe^{3+} and Ta^{5+} ions, the position of the phase transition peaks move slightly to the center and the current intensity decreases slightly, which is the characteristics of enhanced relaxor properties. Compositional and chemical disorders contribute to slightly enhanced relaxor properties. And this phenomenon is consistent with the variation of *P*–*E* hysteresis loops.

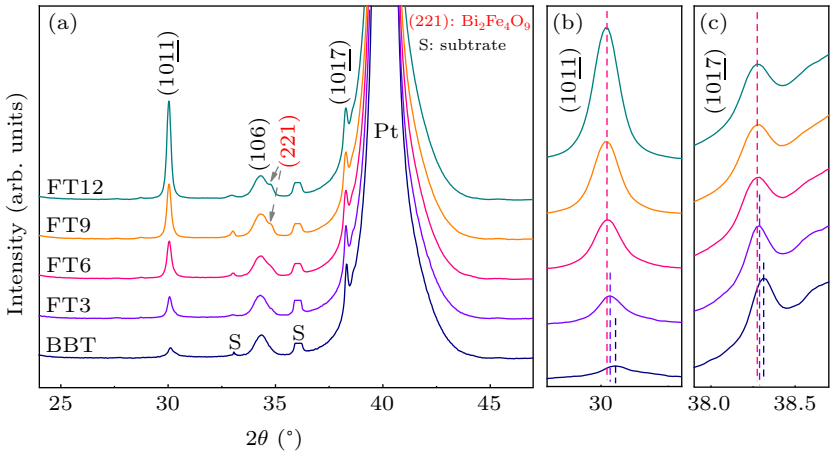


Fig. 2. (a) XRD patterns of BBT, FT3, FT6, FT9, and FT12 films. (b) and (c) Enlarged images of (10$\underline{11}$) and (10$\underline{17}$) peaks, respectively.

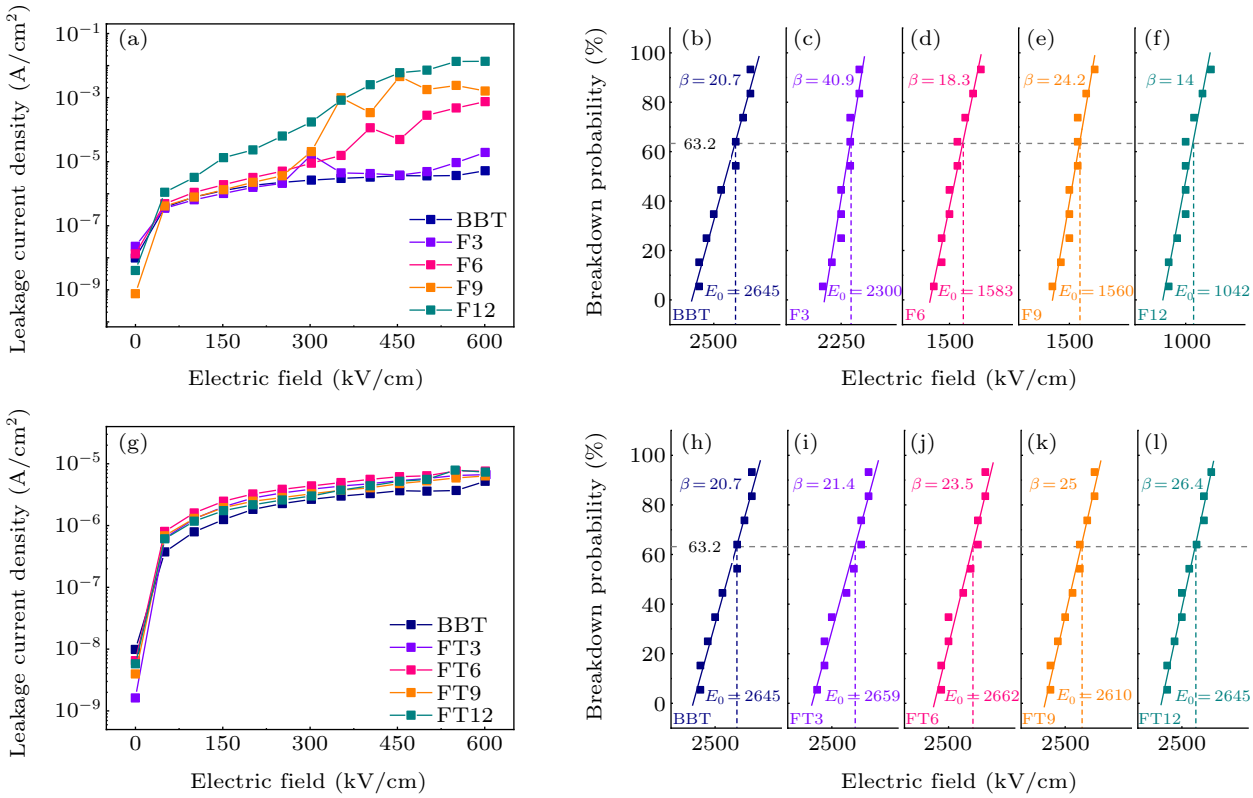


Fig. 3. Leakage current densities of (a) F-series and (g) FT-series films as a function of external electric field. (f) Two-parameter Weibull distribution analysis of the breakdown strengths of (b)–(f) F-series and (h)–(l) FT-series films. E_0 is the characteristic breakdown strength.

As is known to all, the doping of Fe^{3+} ions is easy to introduce oxygen vacancies in the film because of the valence state of Fe^{3+} ion is smaller than that of Ti^{4+} ion.[20,30] On the one hand, the defect dipoles formed by Fe^{3+} ions and oxygen vacancies contribute to the improvement of polarization.[20,27] However, on the other hand, the oxygen vacancy itself is a defect with net charge, which easily leads to an increase in leakage current. What is more, the oxygen vacancies also affect the height of potential barrier between the electrode and film, which makes the electrode injection behavior easier to occur.[31] As is shown in Fig. 3(a), BBT film has a good leakage properties. The leakage current density is about

10^{-6} A/cm^2 when the external electric field is 600 kV/cm. With the increase of Fe^{3+} content, the leakage current density gradually increases to $\sim 10^{-1}$ A/cm^2. Such a significant increase in leakage current density is detrimental to the breakdown strength of the films. The characteristic breakdown electric field E_0 derived from Weibull distribution is a parameter that can be used to evaluate the breakdown strength of a film (Figs. 3(b)–3(f)).[32] The E_0 of F-series are 2645, 2300, 1583, 1560, and 1042 kV/cm. After Ta^{5+} ion continues to be introduced into the system, the leakage performance is greatly improved compared with the Fe-doped films due to the charge balance (Fig. 3(g)). The leakage current densities of all FT-series films are very similar. And the E_0 of FT-series films are stable at about 2600 kV/cm. What is more, All β values of F-series and FT-series films show that the film has a good uniformity.

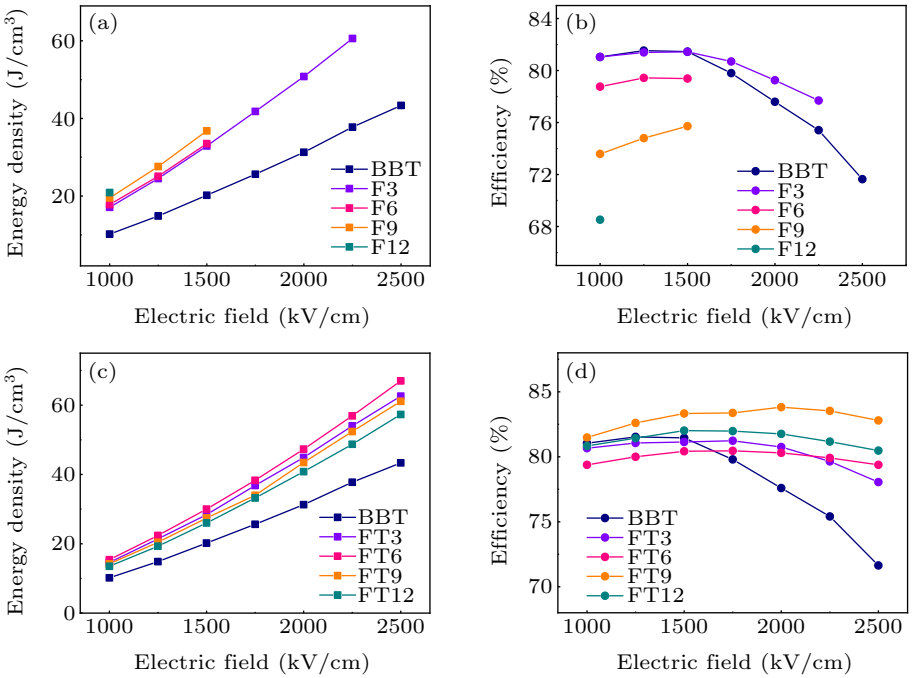


Fig. 4. Energy storage performance of (a), (b) F-series and (c), (d) FT-series films.

The *P*–*E* hysteresis loops of F-series and FT-series films under different external electric fields including the highest external electric field are shown in Fig. S2. The E_m of F-series films are significantly reduced, they are 2500, 2250, 1500, 1500, and 1000 kV/cm. However, for FT-series films, they both have a E_m of 2500 kV/cm. The P_m of all (FeTa)-doped films is improved relative to BBT film. And the shape of hysteresis loops has become thinner. Their energy storage performance is shown in Fig. 4. The energy density represents the energy density that can be recovered and is labeled W_{rec}. The optimal W_{rec} of F-series films are 43.3, 60.6, 33.5, 36.8, and 20.9 J/cm^3 with the efficiency of 71.6%, 77.7%, 79.4%, 75.7%, and 68.5%, respectively, under the E_m of 2500, 2250, 1500, 1500, and 1000 kV/cm. Only the energy storage performance of F3 film has been improved due to the greatly improved polarization, which mask the negative effects of the reduced breakdown strength. For films with more Fe^{3+} ions doping, the significantly reduced breakdown strength makes the energy storage performance almost lost. However, for FT-series films, the energy storage performance of all doped films have been all-side improved. The optimal W_{rec} are 43.3, 62.6, 67, 61.1, and 57.3 J/cm^3 with the efficiency of 71.6%, 78.1%, 79.5%, 82.8%, and 80.5%, respectively, under the same E_m of 2500 kV/cm. The W_{rec} of FT6 (67 J/cm^3) is increased by 54.7% compared with BBT (43.3 J/cm^3) film. The BBT film prepared by Yang *et al.* achieved a W_{rec} of 41.2 J/cm^3 with an efficiency of 79.1%. They further prepared a composite films composed of BBT and $BiFe_{0.93}Mn_{0.07}O_3$ with high polarization. However, the W_{rec} still does not exceed 53 J/cm^3.[23] The energy storage performance of BBT film co-doped with Fe^{3+} and Ta^{5+} ion has been significantly improved. Such an obvious improvement can be attributed to two aspects. On the one hand, Fe^{3+} ion and Ta^{5+} ion have larger radius than Ti^{4+} ion leading to an increase in polarization. On the other hand, Fe^{3+} ion and Ta^{5+} ion co-doping leads to the increase of relaxor properties caused by compositional and chemical disorder. In previous studies, La^{3+} and Pr^{3+} ions are usually chosen as dopants. The relaxor properties of doped systems are improved, but the P_m under the same external electric field is significantly reduced. The improved energy storage performance is due to the enhanced breakdown strength. However, the excessively high applied electric field easily leads to the occurrence of electrode injection behavior and reduces the safety. For example,

Yang *et al.* prepared La-doped $Pb_{1-x}La_x(Zr_{0.52}Ti_{0.48})O_3$ films with dopant concentrations of up to 12%.[33] As the concentration of La^{3+} increases from 0 to 12%, the relaxor properties of the films are improved. However, the P_m at an external electric field of 1000 kV/cm decreases from 47 μC/cm^2 to 30 μC/cm^2. Finally, the reason why the W_{rec} of the $Pb_{0.92}La_{0.08}(Zr_{0.52}Ti_{0.48})O_3$ film (27.5 J/cm^3) is higher than that of the $Pb(Zr_{0.52}Ti_{0.48})O_3$ (10.4 J/cm^3) film is because the E_m of the former (1200 kV/cm) is significantly higher than that of the latter (2200 kV/cm). In fact, the vast majority of previous studies have shown that it is difficult to achieve simultaneous enhancement of relaxor properties and P_m under the same external electric field, whether in doped systems, composite systems, or solid solution systems. Based on the results of this work, a strategy of co-substituting the B-site ions with multiple ions with larger radius may give better results.

Frequency stability and temperature stability are important indexes of dielectric film capacitors in practical application. Good stability allows the capacitor to operate at wide range of frequencies and temperatures. Stability tests of FT-series films were performed at an external electric fields of 2000 kV/cm. *P–E* hysteresis loops of FT-series films at frequency of 200, 500, 1000, 1500, and 2000 Hz are shown in Fig. S3. The W_{rec} of all films hardly changed with the increase of frequency. The efficiency of BBT film responds slightly to frequency changes. This response becomes smaller and smaller with the increase of (FeTa) content. This should be attributed to the slightly increased relaxor properties. *P–E* hysteresis loops of FT-series films at different temperatures are shown in Fig. S4. The hysteresis loops of BBT film change obviously when the temperature rises from 20 °C to 80 °C. This result in the efficiency drops from 75.1% to 60.7%. This may be related to the increase in leakage current density at high temperatures. For co-doped films, their energy storage density and efficiency change slightly in the temperature range of 20 °C to 120 °C, which shows an excellent temperature stability.

4. Conclusion

In summary, we compare the effects of Fe^{3+} ion doping and Fe^{3+} and Ta^{5+} ions co-doping on the energy storage performance of $Ba_2Bi_4Ti_5O_{18}$ films. The results show that the polarization of the Fe-doped films under same external electric fields increases dramatically because the radius of Fe^{3+} is larger than that of Ti^{4+}. The leakage current density increases significantly with the increase of Fe^{3+} content resulting in a significant decrease in breakdown strength. What is more, Fe^{3+} doping stabilizes the long-range ferroelectric order, which greatly reduces the efficiency under the same external electric field. However, the co-doping of Fe^{3+} and Ta^{5+} ions not only improves the polarization of BBT film, but also enhances the relaxor properties. These lead to an overall improvement in the energy storage performance of co-doped film. The W_{rec} of $Ba_2Bi_4Ti_{4.94}(FeTa)_{0.06}O_{18}$ film is 67 J/cm^3 with efficiency of 79.5% under external electric field of 2500 kV/cm, which is a significant increase compared with the W_{rec} (43.3 J/cm^3) and efficiency (71.6%) of $Ba_2Bi_4Ti_5O_{18}$ film under same external electric field. Moreover, all films co-doped with Fe^{3+} and Ta^{5+} ions show stable energy storage performance in the frequency range of 200 Hz to 2000 Hz and temperature range of 20 °C to 120 °C. This results show that Ta^{5+} and Fe^{3+} with larger radius together replace Ti^{4+} is an effective way to enhance energy storage performance of BBT film.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 12074204, 11864028, and 11904054) and the Natural Science Foundation of Inner Mongolia, China (Grant No. 2022ZD06).

References

[1] Zhang W, Wang C, Lian J W, Jiang J and Jiang A Q 2021 *Chin. Phys. Lett.* **38** 017701
[2] Chen G G, Lan J, Min T and Xiao J 2021 *Chin. Phys. Lett.* **38** 087701
[3] Zhu L, Zhu X L, Liu X Q and Chen X M 2021 *Chin. Phys. Lett.* **38** 047701
[4] Zheng Q F, Li Q, Xue S D, Wu Y H, Wang L J, Zhang Q, Qin X M, Zhao X Y, Wang F and Yang W G 2021 *Chin. Phys. Lett.* **38** 026102
[5] Hua C Q, Bai H, Zheng Y, Xu Z A, Yang S A, Lu Y H and Wei S H 2021 *Chin. Phys. Lett.* **38** 077501
[6] Ye Q, Shen Y H and Duan C G 2021 *Chin. Phys. Lett.* **38** 087702
[7] Zhao W, Fu Z Q, Deng J M, Li S, Han Y F, Li M R, Wang X Y and Hong J W 2021 *Chin. Phys. Lett.* **38** 037701
[8] Pan H, Lan S, Xu S Q, Zhang Q H, Yao H B, Liu Y Q, Meng F Q, Guo E J, Gu L, Yi D, Wang X R, Huang H, MacManus-Driscoll J L, Chen L Q, Jin K J, Nan C W and Lin Y H 2021 *Science* **374** 100
[9] Wu Q, Wu X, Zhao Y S and Zhao S F 2020 *Chin. Phys. Lett.* **37** 118401
[10] Pan H, Ma J, Ma J, Zhang Q, Liu X, Guan B, Gu L, Zhang X, Zhang Y J, Li L, Shen Y, Lin Y H and Nan C W 2018 *Nat. Commun.* **9** 1813
[11] Zhang T D, Li W, Zhao Y, Yu Y and Fei W D 2018 *Adv. Funct. Mater.* **28** 1706211
[12] Yang L T, Kong X, Li F, Hao H, Cheng Z X, Liu H X, Li J F and Zhang S J 2019 *Prog. Mater. Sci.* **102** 72
[13] Wu Q, Zhao Y, Zhou Y P, Chen X H, Wu X and Zhao S F 2021 *J. Alloys Compd.* **881** 160576
[14] Yan T L, Chen B, Liu G, Niu R P, Shang J, Gao S, Xue W H, Jin J, Yang J R and Li R W 2017 *Chin. Phys. B* **26** 067702
[15] Zou C, Chen B, Zhu X J, Zuo Z H, Liu Y W, Chen Y F, Zhan Q F and Li R W 2011 *Chin. Phys. B* **20** 117701
[16] Lin P T, Li X, Zhang L, Yin J H, Cheng X W, Wang Z H, Wu Y C and Wu G H 2014 *Chin. Phys. B* **23** 047701
[17] Wu Q, Wu X and Zhao S F 2020 *Appl. Phys. A* **126** 883
[18] Song B J, Wu S H, Li F, Chen P, Shen B and Zhai J W 2019 *J. Mater. Chem. C* **7** 10891
[19] Shvartsman V V, Lupascu D C and Green D J 2012 *J. Am. Ceram. Soc.* **95** 1
[20] Pan Z B, Wang P, Hou X, Yao L M, Zhang G Z, Wang J, Liu J J, Shen M, Zhang Y J, Jiang S L, Zhai J W and Wang Q 2020 *Adv. Energy Mater.* 2001536
[21] Cao J, Koval V, Zhang H F, Lin Y Y, Wu J Y, Meng N, Li Y, Li Z, Zhang H T and Yan H X 2019 *J. Eur. Ceram. Soc.* **39** 1042
[22] Yang B B, Guo M Y, Tang X W, Wei R H, Hu L, Yang J, Song W H, Dai J M, Lou X J, Zhu X B and Sun Y P 2019 *J. Mater. Chem. C* **7** 1888

[23] Yang B B, Guo M Y, Li C H, Song D P, Tang X W, Wei R H, Hu L, Lou X J, Zhu X B and Sun Y P 2019 *Appl. Phys. Lett.* **115** 243901

[24] Ghosh D C and Biswas R 2003 *Int. J. Mol. Sci.* **4** 379

[25] Wang J J, Wu P P, Ma X Q and Chen L Q 2010 *J. Appl. Phys.* **108** 114105

[26] Huang Y H, Wang J J, Yang T N, Wu Y J, Chen X M and Chen L Q 2018 *Appl. Phys. Lett.* **112** 102901

[27] Zhang H Z, Zhou J, Chen W, Yang X, Shen J and Wu C L 2017 *J. Electron. Mater.* **46** 6167

[28] Raghavan C M, Kim J W, Kim S S and Kim J W 2014 *J. Sol-Gel Sci. Technol.* **73** 403

[29] El-Bey A, El Bahraoui T, Taibi M, Belayachi A, Abd-Lefdil M, El-Naggar A M, Albassam A A, Fedorchuk A O, Lakshminarayana G, Czaja P and Kityk I V 2016 *J. Alloys Compd.* **684** 412

[30] Fuentes S, Muñoz P, Barraza N, Chávez-Ángel E and Sotomayor Torres C M 2015 *J. Sol-Gel Sci. Technol.* **75** 593

[31] Xie Y J, Hao H, Huang Z T, Zhang S, Cao M H, Yao Z H and Liu H X 2021 *J. Alloys Compd.* **884** 161031

[32] Pan H, Li F, Liu Y, Zhang Q H, Wang M, Lan S, Zheng Y P, Ma J, Gu L, Shen Y, Yu P, Zhang S J, Chen L Q, Lin Y H and Nan C W 2019 *Science* **365** 578

[33] Dang H T, Trinh T T, Nguyen C T, Do T V, Nguyen M D, Vu H N 2019 *Mater. Chem. Phys.* **234** 210