

Enhanced energy storage performance in NBT-based MLCCs via cooperative optimization of polarization and grain alignment

Corresponding Author: Professor Fei Li

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This paper contains important information for related researchers as it presents a method to maximize energy storage efficiency using defect control and crystal orientation techniques in NBT-SBT materials. This paper can be published after revision, but corrections/explanations are required for the following matters:

1. The sentence "This disparity can be attributed to the lower electrostriction coefficient Q33 of ABO₃ perovskite crystals in the <111> direction compared to other directions" on line 252 requires appropriate references and a more detailed explanation. Samples textured in the <111> direction have a smaller polarization value than other samples but have a higher energy storage capacity because they have strong dielectric breakdown strength and can withstand a high electric field. Therefore, in this paper, it is considered very important to analyze why samples aligned in the <111> direction have high dielectric breakdown strength. The authors need to provide a more detailed analysis and explanation on this part. They claim that, in general, the electric strain coefficient (Q33) in the <111> direction in the perovskite structure is smaller than in other directions. However, in the perovskite structure, the electric strain coefficient along the direction may vary depending on the crystal structure (rhombohedral, orthorhombic, tetragonal, etc.). Therefore, a more detailed explanation is needed regarding the crystal structure and direction-dependent electrical strain characteristics of the BNT-BST material synthesized in this study. Additionally, another reason why the dielectric breakdown strength of the perovskite structure varies depending on the crystal direction may be the difference in atomic density and interatomic bonding force depending on the crystal direction. The authors need to provide a more logical explanation as to why the <111> oriented samples have higher dielectric strength than randomly oriented samples or ceramic samples with crystals oriented in the <001> direction. One of the important technologies in future ceramic processing is crystal orientation technology. Changes in dielectric breakdown characteristics and the electrical properties of ceramics oriented in various crystal directions are crucial information in the ceramic device industry. Therefore, a more detailed and logical explanation is needed.

2. In Figure 5(e), it was calculated that the sample in the <111> direction had a higher W_{rec} value than the sample in the <001> direction under the same electric field conditions. However, in the P-E loop in Figure 5(a), the polarization value of the sample in the <111> direction is smaller than the polarization value of the sample in the <001> direction. How can a sample in the <111> direction have a higher W_{rec} value than a sample in the <001> direction under the same electric field?

3. Since NBT is a single phase, it would be better to express it as Na_{1/2}Bi_{1/2}TiO₃ rather than Na_{0.5}Bi_{0.5}TiO₃.

4. Since the MLCC samples also have the composition of 0.65NBT-0.35SBT doped with Mn, it would be appropriate to express "0.65NBT-0.35SBT matrix" in line 247 of the text as "0.5 mol% Mn-doped 0.65NBT-0.35SBT matrix".

5. The authors represented the recoverable energy storage density as follows:

$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} (P_r)^{\alpha} (P_{\text{max}})^{1-\alpha} dP$$

This is an incorrect mathematical formula for W_{rec}. Although the positive integral of an electric field with respect to polarization from remnant polarization (P_r) to saturated polarization (P_{max}) seems to be identical to the negative integral of

an electric field with respect to polarization from $P_{\max}$ to P_r mathematically, the positive integral cannot be equal to the negative integral due to the hysteretic characteristic of ferroelectrics/piezoelectrics in reality. As the authors probably know, the upward path in a hysteresis loop from P_r to $P_{\max}$ is never identical to the downward path from $P_{\max}$ to P_r . Hence, W_{rec} should be represented as shown in [Ceram. Inter. 47 (2021) 23488; Adv. Funct. Mater 29 (2019) 1807321]:
 $W_{\text{rec}} = -\int_{P_{\max}}^{P_r} E dP$

6. When synthesizing from $\langle 111 \rangle$ -BaTiO₃ templates to $\langle 111 \rangle$ -SrTiO₃ templates using the topochemical reaction method, Ba compound residues will remain. Also, when synthesizing from Bi₄Ti₃O₁₂ templates to $\langle 001 \rangle$ -SrTiO₃ templates, Bi compound residues will remain. How did the author remove these residual compounds?

7. Sometimes, the characteristics of the final synthesized material may vary depending on the difference in starting materials. Therefore, it is necessary to provide the manufacturer and model name of the starting materials for synthesizing Mn-doped NBT-SBT ceramic and $\langle 001 \rangle$ - and $\langle 111 \rangle$ -SrTiO₃ template particles.

Reviewer #2

(Remarks to the Author)

The manuscript is well written and has scientific interest. It may be accepted in its present form.

Reviewer #3

(Remarks to the Author)

Manuscript Title: Enhanced energy storage density and efficiency in NBT-based MLCCs via a cooperative optimization of polarization and grain alignment

Authors: Yang Li, Ningbo Fan, Jie Wu, Bin Xu, Xuexin Li, Xuechen Liu, Yizhou Xiao, Dingwei Hou, Xinya Feng, Jinjing Zhang, Shujun Zhang, Jinglei Li & Fei Li

Authors have prepared $(1-x)(0.65\text{Na}0.5\text{Bi}0.5\text{TiO}_3-0.35\text{Sr}0.7\text{Bi}0.2\text{TiO}_3)-x\text{MnO}_2$ ($x = 0, 0.5 \text{ mol\%, } 1 \text{ mol\%, and } 1.5 \text{ mol\%}$) using solid-state reaction method. Four ceramics samples were characterised by XPS, EPR, P-E loop, dielectric measurements as a function frequency and temperature, XRD patterns as a function of temperature, Rietveld refinements for RT-XRD data and Raman spectra. Based on the increase in polarisation maximum, decrease in remnant polarisation and decrease in hysteresis loss, $x=0.5 \text{ mol\% MnO}_2$ substituted sample was selected to further optimisation of the energy storage density. For this, non-textured, $\langle 001 \rangle$ -textured and $\langle 111 \rangle$ - textured MLCC capacitors with 5 effective layers were prepared through tedious preparation process and analyzed by XRD pattern, SEM micrographs, elemental mapping, EBSD, P-E loop, S-E loop, breakdown strength and discharge-time curves. W_{rec} , E_b and W_{dis} were calculated. Further, temperature dependent (-100 to 200°C) unipolar P-E loop and fatigue performance up to 10^6 cycles were also measured.

The main results of the manuscript are that 5 wt% SrTiO₃ flakes added $\langle 111 \rangle$ -textured MLCC capacitors exhibit η , E_b and W_{dis} respectively 95%, 850 kV/cm and 15.7 J/cm³ (Figure 5(i)) and the main finding is that increasing the breakdown strength (E_b) through texturing plays a major role to improve the energy storage density rather than increase of $P_{\max}$. For achieving ultrahigh energy storage density and efficiency, the manuscript may be considered with a mandatory major revision.

(1) DFPT calculation was carried out to obtain changes in the polarisation due to Mn-substitution. A 2x2x2 supercell with 40 atoms and 8 Formula units were taken for the calculation. The calculation was done for the composition Na_{0.5}Bi_{0.5}Ti_{0.875}Mn_{0.125}O₃. However, from the experiments, the best results were obtained for 0.995(0.65Na_{0.5}Bi_{0.5}TiO₃-0.35Sr_{0.7}Bi_{0.2}TiO₃)-0.005MnO₂ composition. Experimental composition and computational composition are in no way close to each another. Sr was not included for the calculation. Authors should have taken Na_{0.32}Bi_{0.38}Sr_{0.24}Ti_{0.995}Mn_{0.005}O₃ as the composition for computation. Four Bi, two Na and two Sr should have taken for each unit cell. Further, 6x6x6 supercell, one Ti may be replaced by Mn. This could be a close composition for the calculation to match the experimental composition and to explain the experimental observation. Enthalpy of formation for Mn²⁺, Mn³⁺, Mn⁴⁺, Ti³⁺ and Ti⁴⁺ should be comparable and this data was not given in the manuscript to ascertain that on Mn²⁺ substitution, system is a minimum energy configuration. Mn²⁺ substitution improves the polarisation is not universal result that can be applied for all perovskite systems. Therefore, computational results and experimental results may not be connected for discussion, even if the authors' write "as an example" (page 6, line 106). Therefore, computational results and the relevant discussion should be completely removed from the manuscript and accordingly whole of the manuscript may be revised.

(2) Was there a Mn peak in XPS? Please include it in the manuscript (or) supplementary.

(3) Large number of pores is seen in the SEM cross-section micrograph in both textured samples. Why pores are formed at large numbers in textured sample compared to non-textured sample? How to study the impact of pores on the energy storage density?

Reviewer #4

(Remarks to the Author)

The paper of Yang Li et al. "Enhanced energy storage density and efficiency in NBT-based MLCCs via a cooperative optimization of polarization and grain alignment" presents a synergistic optimization strategy that combine polarization and grain alignment engineering. As per my observation, the manuscript over all is well written and the experimental results are well analyzed. However, the manuscript needs a revision to address several points list below before I could recommend it for publication. The comments are listed below:

Comment 1: Born effective charge of Mn²⁺ (2.66 e) is smallest among the Ti³⁺, Ti⁴⁺, Mn⁴⁺, Mn³⁺ and the binding energy is maximum. Then, Why Mn²⁺ causes such a significant increase in off-centering displacements compared to Mn⁴⁺ and Mn³⁺?

Comment 2: How were the different valence states of Mn (Mn⁴⁺, Mn³⁺, and Mn²⁺) confirmed experimentally under high-temperature sintering conditions?

Comment 3: It is noted that Mn doping at 0.5 mol% results in the highest Ti⁴⁺ content, with subsequent doping levels gradually reducing Ti⁴⁺ but still maintaining levels higher than the undoped sample.

Comment 4: In EPR, authors claim 0.5 mol% Mn doped component shows only one type of signal, corresponding to Mn²⁺ and 1 mol% Mn exhibits both Mn²⁺ and Mn⁴⁺ signals. It is difficult to distinguish the between the EPR of 0.5% and 1.0% spectrum. How were Mn²⁺ and 4+ valence states identified in the 1 mol% Mn doped? Could the authors elaborate on the characteristics of this signal and why it is specific to Mn²⁺ in 0.5 mol%?

Comment 5: How does the presence of a secondary phase and changes in grain orientation specifically affect the hysteresis and energy storage performance of Mn-doped 0.65NBT-0.35SBT?

Comment 6: In figure 3d, with the % of Mn doping the dielectric constant increases. What is the reason for this enhancement of dielectric constant?

Comment 7: The Temperature dependent dielectric curve shows broadness and frequency dependent behaviour which is the characteristics of relaxor ferroelectric. The author could calculate the diffusivity parameter to estimate the relaxor nature and relate with the polarization behaviour of samples.

Comment 8: What is the reason for synthesizing flaky Ba₆Ti₁₇O₄₀ precursor to acquire the <111>-oriented SrTiO₃ flake microcrystalline template?

Comment 9: Describe the relationship between the structural variation of <100> and <111> and the difference in polarization values between them.

Comment 10: Perhaps the authors could have also cite other relevant articles, such as EPR and magnetization studies of the manganites (<https://doi.org/10.1016/j.jmmm.2020.167450>), <https://doi.org/10.1088/2053-1591/2/9/096301>, and <https://doi.org/10.1063/1.4804940>,

DOI 10.1088/1361-6463/aa7fa7, <https://doi.org/10.1063/1.4862169> etc.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have provided thorough and meaningful responses to the reviewers' comments and have revised the manuscript accordingly. Therefore, the paper is deemed suitable for publication.

Reviewer #3

(Remarks to the Author)

The main point raised in the review report was that "Why DFPT calculation was not carried out on a composition close to that of experimental composition?". Authours have pointed out that the DFPT calculation was carried out on Na_{1/2}Bi_{1/2}TiO₃ as it is major component (65%) and also due to the computational challenge involved in terms of reasonably large super cell to match the experimental composition. Further, the computational result is that Mn²⁺ substitution improves the polarisation. This result was compared only qualitatively to the selected experimental composition. Authours reply may be considered positively.

Reviewer #4

(Remarks to the Author)

Authors have addressed the comments in details. It can be accepted.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

Electronic Materials Research Laboratory, Xi'an Jiaotong University

Add: 28 Xianning West Road, Xi'an, 710049, Shaanxi province, P. R. China

E-mail: ful5@xjtu.edu.cn

Sep 2, 2024

Dear reviewers,

Thank you very much for reviewing our manuscript and we appreciate the positive comments and valuable suggestions by which the quality of this revised manuscript is greatly improved. We have revised our manuscript accordingly, the point-by-point responses to comments are enclosed in this letter, please kindly double check. We hope our manuscript is now in good shape and address all your concerns and questions.

Reviewer #1:

This paper contains important information for related researchers as it presents a method to maximize energy storage efficiency using defect control and crystal orientation techniques in NBT-SBT materials. This paper can be published after revision, but corrections/explanations are required for the following matters:

1. The sentence “This disparity can be attributed to the lower electrostriction coefficient Q_{33} of ABO_3 perovskite crystals in the $\langle 111 \rangle$ direction compared to other directions” on line 252 requires appropriate references and a more detailed explanation. Samples textured in the $\langle 111 \rangle$ direction have a smaller polarization value than other samples but have a higher energy storage capacity because they have strong dielectric breakdown strength and can withstand a high electric field. Therefore, in this paper, it is considered very important to analyze why samples aligned in the $\langle 111 \rangle$ direction have high dielectric breakdown strength. The authors need to provide a more detailed analysis and explanation on this part. They claim that, in general, the electric strain coefficient (Q_{33}) in the $\langle 111 \rangle$ direction in the perovskite structure is smaller than in other directions. However, in the perovskite structure, the electric strain coefficient along the direction may vary depending on the crystal structure (rhombohedral, orthorhombic, tetragonal, etc.). Therefore, a more detailed explanation is needed regarding the crystal structure and direction-dependent electrical strain characteristics of the BNT-BST material synthesized in this

study. Additionally, another reason why the dielectric breakdown strength of the perovskite structure varies depending on the crystal direction may be the difference in atomic density and interatomic bonding force depending on the crystal direction. The authors need to provide a more logical explanation as to why the $\langle 111 \rangle$ oriented samples have higher dielectric strength than randomly oriented samples or ceramic samples with crystals oriented in the $\langle 001 \rangle$ direction. One of the important technologies in future ceramic processing is crystal orientation technology. Changes in dielectric breakdown characteristics and the electrical properties of ceramics oriented in various crystal directions are crucial information in the ceramic device industry. Therefore, a more detailed and logical explanation is needed.

Author's response:

Thank you very much for your comment. Electrostriction is present in all crystal symmetries because it is a fourth rank polar tensor. Electrostriction is a measure of the polarization induced by ions shifting away from their natural equilibrium positions, giving rise to variations in the lattice parameters. A typical potential of an ion-pair is shown in Figure R1, where the energy required to compress the ion-pair is higher than the energy required to extend the ion pair [N. W. Ashcroft and N. D. Mermin, Solid State Physics (Brooks Cole, Philadelphia, 1976); C. Kittel, Introduction to Solid State Physics, 8th ed. (Wiley, New York, 2004)]. Based on the potential characteristics, the relative displacement between positive and negative ions is prone to occur via extension of the lattice instead of compression.

[Figure redacted]

Figure R1. Schematic figure of the pair potential in ionic crystal, where represents the equilibrium distance between positive and negative ions. [Applied Physics Reviews 1, 011103 (2014)]

Figure R2 shows the variation in the oxygen octahedral structure as polarization appeared

along different crystallographic directions. When a B-site cation moves along the [001] direction, an oxygen anion O_1 will be “pushed” upward to release the energy that originated from compressing the distance of B- O_1 , as shown in Figure R2(b). Consequently, the lattice parameter along the [001] direction is elongated by d . The strain along the [001] direction can be expressed as d/a .

[Figure redacted]

Figure R2. The deformation of oxygen-octahedral structure with different polarization directions. (a) Zero polarization; (b) polarization along [001] direction; (c) polarization along [110] direction; (d) polarization along [111] direction. The red arrows for oxygen ions indicate that the oxygen ions move along the polarization direction. The purple arrows for oxygen ions indicate that oxygen ions move along the direction perpendicular to the polarization direction. [Applied Physics Reviews 1, 011103 (2014)]

Figure R2(c) shows the scenario where a B-site cation moves along the [110] direction. In this case, the oxygen O_3 and O_4 anions will move along the [110] or $[1\bar{1}0]/[\bar{1}10]$ directions to release the B- O_3 and B- O_4 pair potential because the direction of B-O bond ($\langle 100 \rangle$) is not parallel to the [110] direction. It should be noted that the electrostrictive coefficient Q_{33} along the [110] direction is reduced by the motion of the O_3/O_4 ions along the $[1\bar{1}0]/[\bar{1}10]$ directions, because the $[1\bar{1}0]/[\bar{1}10]$ directions are perpendicular to the [110] direction.

Analogous to the [110] direction, a similar scenario occurs for the [111] direction, as shown in Figure R2(d). As a B-site cation moves along the [111] direction, the oxygen ions can move along the directions perpendicular to [111] direction to release the B-O pair potential, which

mitigates the Q_{33} along the $[111]$ direction. The difference between the $[111]$ and $[110]$ directions is that in the former, the oxygen ions are easier to move along the perpendicular direction to release the compression energy. This is because the angle between the $[111]$ and B-O chain directions is 54° , which is larger than the angle between the $[110]$ and B-O bond directions (45°). Based on this approach, electrostrictive anisotropy of perovskite crystals has been explained qualitatively, which is related to the oxygen octahedral structure. The maximum electrostrictive coefficient Q_{33} is along the $\langle 001 \rangle$ direction because the B-O chains align along the $\langle 111 \rangle$ direction. The minimum Q_{33} is along the $\langle 111 \rangle$ direction because the B-O chains have a larger angle with the $\langle 111 \rangle$ direction.

From a mechanical perspective, the strains and elastic energies induced by applied electric fields heavily impact the electromechanical breakdown strength of dielectric ceramics. Perovskite ceramics are considered brittle solids and thus easily generate microcracks under tensile strains, which may greatly increase the breakdown probability of dielectric ceramics. A high level of tensile strain is expected to induce severe microcracks inside the dielectrics, and is thought to be one of the main reasons that the breakdown strength of perovskite ceramics has reached a plateau over the years. Thus, reducing the field-induced strains is highly desired for further enhancing the energy density of perovskite materials. In perovskite ceramics, the maximum Q_{33} is along the $\langle 001 \rangle$ direction, and the minimum Q_{33} is along the $\langle 111 \rangle$ direction. $\langle 111 \rangle$ -oriented ceramics have smaller tensile strain and can withstand higher breakdown electric fields than nontextured ceramics and $\langle 001 \rangle$ -oriented ceramics.

We apologize for not providing a detailed explanation regarding the content related to Q_{33} earlier. Now, we have added relevant statements and explanations in the manuscript, and provided relevant references as evidence support. The following content has been added to the manuscript:

The variations in the octahedral oxygen structure within perovskite materials as a function of polarization along different crystallographic directions are shown in Fig. S11 of the *Supplementary Information*. When Ti^{4+} ions at the B site move along the $[001]$ direction, the oxygen ion O_1 is “pushed” upwards, releasing energy due to the compression of the $\text{Ti}-\text{O}_1$ distance. Consequently, the lattice parameter along the $[001]$ direction is extended by a distance d . The strain along the $[001]$ direction is expressed as d/a . When Ti^{4+} ions move along the $[111]$

direction, the oxygen ions can move in a direction perpendicular to the $[111]$ direction, releasing the Ti-O pairs potential and thereby reducing Q_{33} along the $[111]$ direction. Compared to the $[001]$ direction, it is easier for oxygen ions to move perpendicularly along the $[111]$ direction to release compressive energy. Thus, the maximum Q_{33} is observed along the $\langle 001 \rangle$ direction, while the minimum Q_{33} is along the $\langle 111 \rangle$ direction.

2. In Figure 5(e), it was calculated that the sample in the $\langle 111 \rangle$ direction had a higher W_{rec} value than the sample in the $\langle 001 \rangle$ direction under the same electric field conditions. However, in the P - E loop in Figure 5(a), the polarization value of the sample in the $\langle 111 \rangle$ direction is smaller than the polarization value of the sample in the $\langle 001 \rangle$ direction. How can a sample in the $\langle 111 \rangle$ direction have a higher W_{rec} value than a sample in the $\langle 001 \rangle$ direction under the same electric field?

Author's response:

Thank you very much for your comment. The reason why $\langle 111 \rangle$ -oriented samples have higher W_{rec} compared to $\langle 001 \rangle$ -oriented samples under the same electric field is that $\langle 111 \rangle$ -oriented samples exhibit saturation polarization delay.

The value of W_{rec} is influenced not only by P_{max} , but also by P_r , hysteresis, and the degree of delay in saturation polarization (i.e., the time required to reach saturation). Although the polarization value of the sample along the $\langle 111 \rangle$ -orientation is a bit smaller than that along the $\langle 001 \rangle$ -orientation under the same electric field, the P - E loops shown in Figure 5(a) reveal that the saturation polarization in $\langle 111 \rangle$ -oriented samples is delayed compared to $\langle 001 \rangle$ -oriented samples. The prepared samples exhibit a mixture of rhombohedral and tetragonal phases, with the rhombohedral phase as the primary crystalline phase. Under an applied electric field, $\langle 001 \rangle$ -oriented rhombohedral ceramics exhibit a “4R” engineered domain configuration, where the polarization reversal process involves 71° and 109° polarization rotations. In contrast, $\langle 111 \rangle$ -oriented rhombohedral ceramics display a single-domain structure, with an ideal polarization reversal involving a 180° rotation. Therefore, compared to $\langle 001 \rangle$ -oriented samples, $\langle 111 \rangle$ -oriented samples are more challenging to polarize, resulting in a delayed saturation polarization. As a result, compared to $\langle 001 \rangle$ -oriented samples, the $\langle 111 \rangle$ -oriented samples exhibit a greater area under the hysteresis loop, i.e., a higher W_{rec} , for the same electric field

strength.

Based on the above discussion, we have added the following discussion to the analysis section of Figure 5 in the manuscript:

Although the polarization of the <001>-textured samples is slightly higher than that of the <111>-textured samples under the same electric field, the <111>-textured samples exhibit a higher W_{rec} . This is attributed to the delayed saturation polarization of the hysteresis loops in the <111>-textured samples. Under an applied electric field, <001>-oriented rhombohedral ceramics exhibit a “4R” engineered domain configuration, where the polarization reversal process involves 71° and 109° polarization rotations. In contrast, <111>-oriented rhombohedral ceramics display a single-domain structure, with an ideal polarization reversal involving a 180° rotation. Therefore, compared to <100>-oriented samples, <111>-oriented samples are more challenging to polarize, resulting in a delayed saturation polarization.

3. Since NBT is a single phase, it would be better to express it as $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ rather than $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$.

Author’s response:

Thank you very much for your comment. We have modified the chemical formula of single-phase NBT from $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ to $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ according to your suggestion.

4. Since the MLCC samples also have the composition of 0.65NBT-0.35SBT doped with Mn, it would be appropriate to express “0.65NBT-0.35SBT matrix” in line 247 of the text as “0.5 mol% Mn-doped 0.65NBT-0.35SBT matrix”.

Author’s response:

Thank you very much for your comment. We have revised the expression of “0.65NBT-0.35SBT matrix” in line 247 to “0.5 mol% Mn-doped 0.65NBT-0.35SBT matrix”.

5. The authors represented the recoverable energy storage density as follows:

$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} EdP$$

This is an incorrect mathematical formula for W_{rec} . Although the positive integral of an electric

field with respect to polarization from remnant polarization (P_r) to saturated polarization ($P_{\max}$) seems to be identical to the negative integral of an electric field with respect to polarization from $P_{\max}$ to P_r mathematically, the positive integral cannot be equal to the negative integral due to the hysteretic characteristic of ferroelectrics/piezoelectrics in reality. As the authors probably know, the upward path in a hysteresis loop from P_r to $P_{\max}$ is never identical to the downward path from $P_{\max}$ to P_r . Hence, W_{rec} should be represented as shown in [Ceram. Inter. 47 (2021) 23488; Adv. Funct. Mater 29 (2019) 1807321]:

$$W_{\text{rec}} = - \int_{P_{\max}}^{P_r} E dP$$

Author's response:

Thank you very much for your comment. We are very sorry for neglecting the hysteresis characteristics of the P - E loops in the expression of the formula, that is, the positive integral cannot be equal to the negative integral. We have followed your suggestion to modify the expression of the formula to the correct expression, which is $W_{\text{rec}} = - \int_{P_{\max}}^{P_r} E dP$. In addition, we have also cited the references you mentioned in our main text:

[73] Akram, F. *et al.* Thermally-stable high energy-storage performance over a wide temperature range in relaxor-ferroelectric $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ -based ceramics. *Ceramics International* 47, 23488–23496 (2021).

[74] Wang, H., Liu, Y., Yang, T. & Zhang, S. Ultrahigh energy-storage density in antiferroelectric ceramics with field-induced multiphase transitions. *Adv Funct Materials* 29, 1807321 (2019).

6. When synthesizing from $\langle 111 \rangle$ - BaTiO_3 templates to $\langle 111 \rangle$ - SrTiO_3 templates using the topochemical reaction method, Ba compound residues will remain. Also, when synthesizing from $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ templates to $\langle 001 \rangle$ - SrTiO_3 templates, Bi compound residues will remain. How did the author remove these residual compounds?

Author's response:

Thank you very much for your comment. The residual Ba compounds and Bi compounds were effectively removed through repeated ultrasonic cleaning in deionized water and pure nitric acid, respectively.

When synthesizing $\langle 111 \rangle$ -SrTiO₃ templates from $\langle 111 \rangle$ -BaTiO₃ templates, Ba is present as BaCl₂. Because BaCl₂ is highly soluble in water, it can be effectively removed through repeated ultrasonic cleaning with hot deionized water, resulting in pure $\langle 111 \rangle$ -SrTiO₃ templates. In contrast, when synthesizing $\langle 001 \rangle$ -SrTiO₃ templates from Bi₄Ti₃O₁₂ templates, Bi is present as BiCl₃. Since BiCl₃ is soluble in nitric acid, the product must first be cleaned with pure nitric acid to remove BiCl₃. After this, the product should be further cleaned with hot deionized water to ensure complete removal of any remaining contaminants and to obtain pure $\langle 001 \rangle$ -SrTiO₃ templates.

We apologize for the oversight in the initial experimental section. This detailed procedure has now been added to the “Methods” section of the manuscript.

7. Sometimes, the characteristics of the final synthesized material may vary depending on the difference in starting materials. Therefore, it is necessary to provide the manufacturer and model name of the starting materials for synthesizing Mn-doped NBT-SBT ceramic and $\langle 001 \rangle$ - and $\langle 111 \rangle$ -SrTiO₃ template particles.

Author’s response:

Thank you very much for your comment. We have added the manufacturer and model name of the starting materials for synthesizing Mn doped NBT-SBT ceramic and $\langle 001 \rangle$ - and $\langle 111 \rangle$ - SrTiO₃ template particles in the “Methods” of the manuscript.

Reviewer #2:

The manuscript is well written and has scientific interest. It may be accepted in its present form.

Author’s response:

Thank you very much for reviewing our manuscript and we appreciate your positive comments.

Reviewer #3:

Authors have prepared $(1-x)(0.65\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.35\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3)-x\text{MnO}_2$ ($x = 0, 0.5 \text{ mol\%}, 1 \text{ mol\%}, \text{ and } 1.5 \text{ mol\%}$) using solid-state reaction method. Four ceramics samples were characterized by XPS, EPR, P - E loop, dielectric measurements as a function frequency and

temperature, XRD patterns as a function of temperature, Rietveld refinements for RT-XRD data and Raman spectra. Based on the increase in polarization maximum, decrease in remnant polarization and decrease in hysteresis loss, $x = 0.5$ mol% MnO_2 substituted sample was selected to further optimization of the energy storage density. For this, non-textured, $\langle 001 \rangle$ -textured and $\langle 111 \rangle$ -textured MLCC capacitors with 5 effective layers were prepared through tedious preparation process and analyzed by XRD pattern, SEM micrographs, elemental mapping, EBSD, P - E loop, S - E loop, breakdown strength and discharge-time curves. W_{rec} , η , E_b and W_{dis} were calculated. Further, temperature dependent (-100 to 200 °C) unipolar P - E loop and fatigue performance up to 10^6 cycles were also measured.

The main results of the manuscript are that 5 wt% SrTiO_3 flakes added $\langle 111 \rangle$ -textured MLCC capacitors exhibit η , E_b and W_{dis} respectively 95%, 850 kV/cm and 15.7 J/cm^3 (Figure 5(i)) and the main finding is that increasing the breakdown strength (E_b) through texturing plays a major role to improve the energy storage density rather than increase of P_{max} . For achieving ultrahigh energy storage density and efficiency, the manuscript may be considered with a mandatory major revision.

(1) DFPT calculation was carried out to obtain changes in the polarization due to Mn-substitution. A $2 \times 2 \times 2$ supercell with 40 atoms and 8 Formula units were taken for the calculation. The calculation was done for the composition $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.875}\text{Mn}_{0.125}\text{O}_3$. However, from the experiments, the Ti best results were obtained for $0.995(0.65\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - 0.35\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3) - 0.005\text{MnO}_2$ composition. Experimental composition and computational composition are in no way close to each another. Sr was not included for the calculation. Authors should have taken $\text{Na}_{0.32}\text{Bi}_{0.38}\text{Sr}_{0.24}\text{Ti}_{0.995}\text{Mn}_{0.005}\text{O}_3$ as the composition for computation. Four Bi, two Na and two Sr should have taken for each unit cell. Further, $6 \times 6 \times 6$ supercell, one Ti may be replaced by Mn. This could be a close composition for the calculation to match the experimental composition and to explain the experimental observation. Enthalpy of formation for Mn^{2+} , Mn^{3+} , Mn^{4+} , Ti^{3+} and Ti^{4+} should be comparable and this data was not given in the manuscript to ascertain that on Mn^{2+} substitution, system is a minimum energy configuration. Mn^{2+} substitution improves the polarization is not universal result that can be applied for all perovskite systems. Therefore, computational results and experimental results may not be connected for discussion, even if the authors' write "as an example" (page 6, line

106). Therefore, computational results and the relevant discussion should be completely removed from the manuscript and accordingly whole of the manuscript may be revised.

Author's response:

Thank you very much for your comment. We acknowledge your point that using $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.875}\text{Mn}_{0.125}\text{O}_3$ as the composition for calculations would better align with experimental results. The reasons that we used the original composition ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$) for calculations are: (1) Utilizing $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.875}\text{Mn}_{0.125}\text{O}_3$ as the calculation composition would necessitate constructing a supercell with a significantly large number of atoms, and the various atomic positions could result in multiple supercell configurations, presenting a considerable computational challenge. (2) For NBT based ferroelectrics, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ is a major component, thus using $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ as the basis for first-principles calculations can help us to assess the impact of Mn ions on the polarization of NBT-based ceramics.

In determining the stability of the constructed system, we rely on the convergence of computational results. This computational work falls within the domain of computational physics and does not involve calculations related to enthalpy of formation.

The selection of $0.65\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.35\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ as an example for experimental validation is due to its compliance with the requirements for low hysteresis and high polarization in energy storage materials. The doping of Mn ions introduced in this work primarily addresses the issue of reduced polarization in NBT-based ceramics, as highlighted in the introduction, which arises from the volatilization of A-site ions leading to the reduction of Ti^{4+} to Ti^{3+} . We believe that the strategies employed in this study could be applied to other perovskite ceramics with volatile A-site ions for addressing similar polarization reduction issues.

In summary, we really appreciate the reviewer for this very valuable comment, and we agree with the reviewer that using $\text{Na}_{0.32}\text{Bi}_{0.38}\text{Sr}_{0.24}\text{Ti}_{0.995}\text{Mn}_{0.005}\text{O}_3$ as the composition for computation will lead to more accurate and reliable results. However, at current stage, it is very challenge to construct such a complex and reasonable supercell in DFT calculations. In this work, we use $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ as an example to qualitative analyze the impact of Mn on the polarization of NBT-based ferroelectrics.

(2) Was there a Mn peak in XPS? Please include it in the manuscript (or) supplementary.

Author's response:

Thank you very much for your comment. We have conducted numerous XPS tests on the Mn element. Unfortunately, due to the low Mn content, it is hard to obtain a distinctive XPS spectrum for Mn, as shown in the Figure R3. We attempted to perform peak fitting on the 1.5 mol% Mn-doped component and preliminarily determined that it contains three valences: Mn^{2+} , Mn^{3+} , and Mn^{4+} . Considering that the Mn content is too low to obtain accurate XPS data, we don't include XPS results of Mn element in our manuscript.

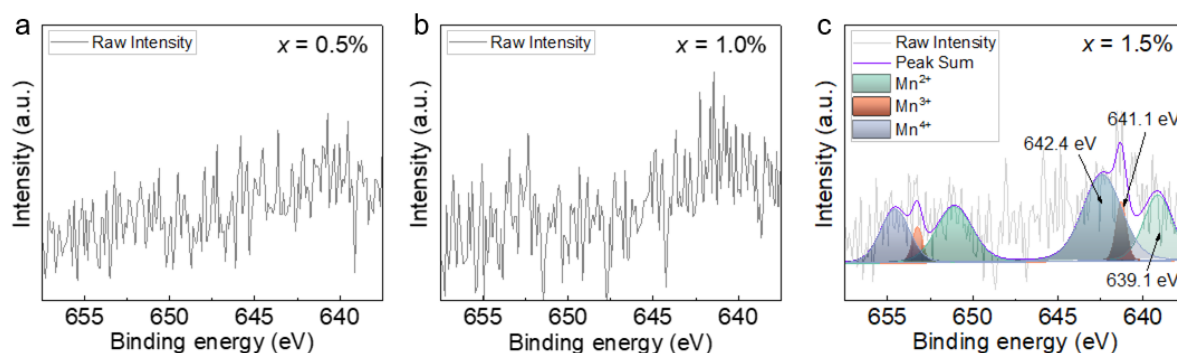


Figure R3. XPS of Mn in NBT-SBT-xMn ceramics: (a) $x = 0.5$ mol%; (b) $x = 1.0$ mol%; (c) $x = 1.5$ mol%.

(3) Large number of pores is seen in the SEM cross-section micrograph in both textured samples. Why pores are formed at large numbers in textured sample compared to non-textured sample? How to study the impact of pores on the energy storage density?

Author's response:

Thank you very much for your comment. The SEM cross-sections of textured samples reveal numerous pores due to two primary reasons: first, during the growth process, the grains in textured samples grow abnormally along specific crystallographic directions, which may result in difficulties to completely fill the pores among grains; second, the grains in textured samples exhibit specific shapes (as illustrated in Figure 4f of the Manuscript), leading to indentations on the fractured surfaces after processing, thereby giving the appearance of pores.

When we try to control crystal orientation in textured ceramics, it is often necessary to sacrifice a certain degree of density, resulting in the presence of pores. In fact, samples with higher density often have higher breakdown electric fields. In order to minimize the influence of pores on the breakdown electric field, we further calcined the sintered textured MLCC in a

mixed atmosphere of argon and oxygen at 1000 °C in a hot isostatic pressing furnace for several hours. The following are the cross-sectional SEM images (Figure R4) of the sintered textured samples before and after heat treatment. Before heat treatment, there were more pores with larger pore sizes, but after heat treatment, the number of pores decreased and the pore size significantly decreased. Therefore, the adverse effect of porosity on energy storage density in textured ceramics can be reduced through heat treatment methods such as hot isostatic pressing and sintering. We have added the SEM images of the cross-section of the <001>-textured samples before and after heat treatment in a mixed atmosphere to Figure S14 in *Supplementary Information* for readers to observe the effect of heat treatment more intuitively.

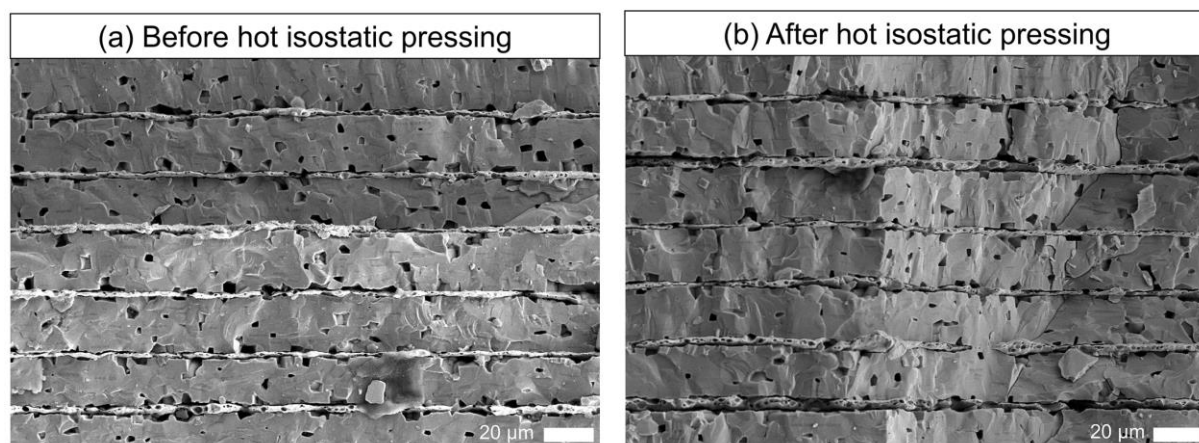


Figure R4. SEM of the cross-section of the <001>-textured samples before and after hot isostatic pressing (added as Figure S14 in *Supplementary Information*).

The impact of pores on energy storage performance can be explored through their effects on both the breakdown electric field and polarization [Prog. Mater Sci. 136, 101101 (2023)]. For example, a research team led by d Y. A. Genenko [J. Phys. D: Appl. Phys. 50, 045303 (2017)] demonstrated that the degree of porosity, pore shape, and orientation serve as levers for tuning the local electric field distribution. Additionally, Chris R. Bowen's group [Acta Materialia 154, 100-112 (2018)] combined experimental and modeling approaches to thoroughly investigate the effects of pore volume fraction and morphology on the polarization response in $(0.5\text{Ba}(\text{Ca}_{0.8}\text{Zr}_{0.2})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3)$ ceramics. The effect of porosity on material properties is intricate and requires a methodical and comprehensive investigation that integrates theoretical simulations with experimental approaches. According to this comment, we shall

systematically study the impact of pores on the performance of textured ceramics in our future work.

Reviewer #4:

The paper of Yang Li et al. “Enhanced energy storage density and efficiency in NBT-based MLCCs via a cooperative optimization of polarization and grain alignment” presents a synergistic optimization strategy that combine polarization and grain alignment engineering. As per my observation, the manuscript over all is well written and the experimental results are well analyzed. However, the manuscript needs a revision to address several points list below before I could recommend it for publication. The comments are listed below:

Comment 1: Born effective charge of Mn^{2+} (2.66 e) is smallest among the Ti^{3+} , Ti^{4+} , Mn^{4+} , Mn^{3+} and the binding energy is maximum. Then, Why Mn^{2+} causes such a significant increase in off-centering displacements compared to Mn^{4+} and Mn^{3+} ?

Author’s response:

Thank you very much for your comment. The reason why Mn^{2+} significantly increases off-centering displacements compared to Mn^{4+} and Mn^{3+} is that Mn^{2+} has the largest ionic radius.

The displacements of the A-site ions, i.e., Na and Bi, are believed to be closely related to ionic radii of the dopants. For instance, the ionic radius of Ti^{4+} , Mn^{4+} , Mn^{3+} , and Mn^{2+} is 0.745, 0.670, 0.720, and 0.970 Å, respectively. The corresponding tolerance factors (defined as $t = \frac{r_{\text{A}} + r_{\text{O}}}{\sqrt{2}(r_{\text{B}} + r_{\text{O}})}$) are shown in Figure R5(a), which exhibit an arc shape with the lowest value given by the Mn^{2+} case ($t = 0.770$) due to its largest size. As depicted in Figure R5(b) and (c), the average displacements of Na and Bi are inversely related to the variation of the tolerance factor.

Qualitatively similar behaviors are also found in the average displacements of Ti, Mn, and O ions, i.e., a decrease followed by an increase by changing the B-site ion from Ti^{4+} to Mn^{4+} , Mn^{3+} , and Mn^{2+} , with the largest value also being from Mn^{2+} . Such similarity can be ascribed to interactions between the displacements of the A-site and the displacements of the B-site or O-site atoms. However, the shape of the curve is slightly different from that of the tolerance factor, e.g., with a minimum at Mn^{3+} instead of Mn^{4+} . This subtlety may be related to the different covalency of the chemical bonds between Mn and O. Note that octahedrally

coordinated Mn^{3+} can have Jahn-Teller distortion (absent in Mn^{4+} and Mn^{2+} cases), but this Jahn-Teller effect is expected to be weak.

Based on the above discussion, we have included Figure S1 and the corresponding analysis in the *Supplementary Information* to illustrate the effect of dopant ionic radius on off-centering displacements. Additionally, we have added the following explanation in the revised manuscript:

The displacements of the A-site ions are believed to be closely related to ionic radii of the dopants. Specifically, Mn^{2+} significantly increases off-centering displacements compared to Mn^{4+} and Mn^{3+} , as Mn^{2+} has the largest ionic radius. The correlation analysis can be found in *Supplementary Information Fig. S1*, along with the corresponding explanation.

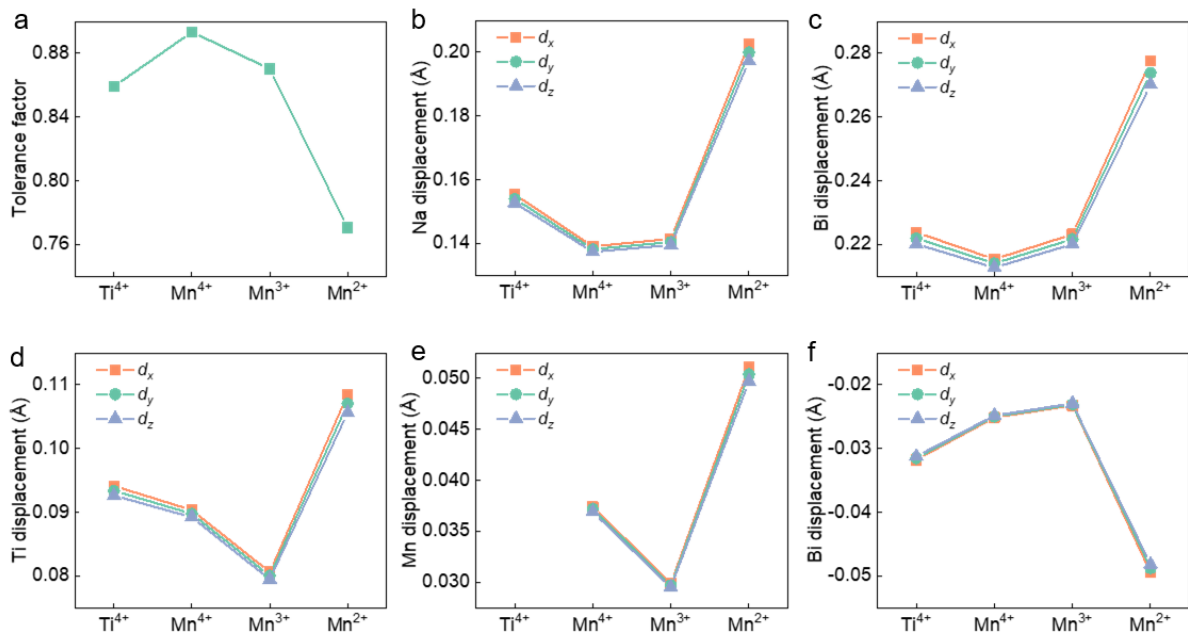


Figure R5 (a) Tolerance factor. (b)-(f) Averaged displacement of Na, Bi, Ti, Mn, and O in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (Ti^{4+}) and Mn^{4+} , Mn^{3+} , and Mn^{2+} doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.875}\text{Mn}_{0.125}\text{O}_3$ (added as Figure S1 in *Supplementary Information*).

Comment 2: How were the different valence states of Mn (Mn^{4+} , Mn^{3+} , and Mn^{2+}) confirmed experimentally under high-temperature sintering conditions?

Author's response:

Thank you very much for your comment. The different valence states of Mn were confirmed through Electron Paramagnetic Resonance (EPR) test results. The samples were prepared by high-temperature sintering, and the EPR test for Mn was conducted at liquid

nitrogen temperature (77 K).

We conducted EPR tests on the 0.5 mol% and 1 mol% Mn doped components, as shown in Figure R6. There are six single peaks in the EPR spectrum shown in Figure R6(a), corresponding to the signal of Mn^{2+} . The six resonance sharp peaks are due to the hyperfine splitting of the Mn isotope nuclear spin of 5/2 [Journal of Physics and Chemistry of Solids 64, 953-960 (2003); J. Mater. Sci.: Mater. Electron. 30, 2953-2965 (2019)]. In the EPR spectrum shown in Figure R6(b), there are six splitting peaks (the enlarged image in the upper right of Figure R6(b) shows the splitting of the peaks), corresponding to the signals of Mn^{2+} and Mn^{4+} ions [J. Appl. Phys. 104, (2008)]. The presence of Mn^{3+} in the 0.5 mol% and 1 mol% Mn doped components cannot be determined based on existing test results, as Mn^{3+} is often referred to as the “EPR silencing” ion, manifests as insignificant zero field splitting, rendering its EPR spectrum undetectable at low frequencies in the conventional X-band (~ 9.5 GHz) [J. Magn. Mater. 519, 167450 (2021)]. However, it can be confirmed that there is no Mn^{4+} in the 0.5 mol% Mn doped component, Mn^{2+} and Mn^{4+} are present in the 1 mol% Mn doped component.

We have redrawn the EPR plot of the 1 mol% Mn doped component in *Supplementary Information* Figure S3, and amplified the first signal splitting peak to facilitate readers’ observation of the data. Additionally, the temperature conditions (liquid nitrogen temperature, 77 K) for Mn EPR measurements have been included in the “Methods” section of the manuscript.

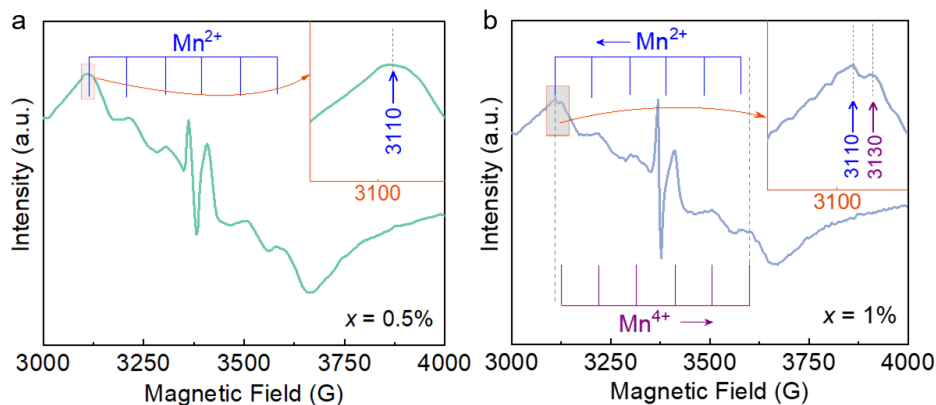


Figure R6. EPR of Mn in NBT-SBT-0.5 mol% Mn and NBT-SBT-1 mol% Mn ceramics.

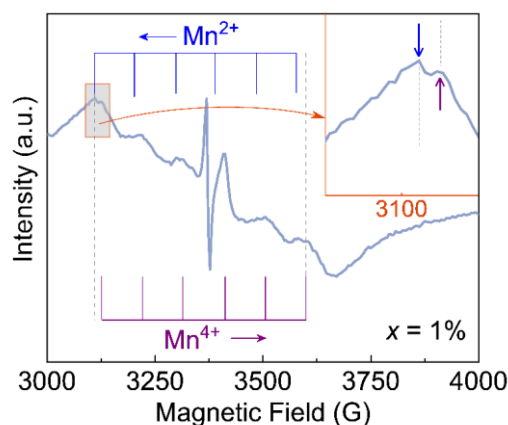


Figure S3 EPR of Mn in NBT-SBT-1 mol% Mn ceramic.

Comment 3: It is noted that Mn doping at 0.5 mol% results in the highest Ti^{4+} content, with subsequent doping levels gradually reducing Ti^{4+} but still maintaining levels higher than the undoped sample.

Author's response:

Thank you very much for your comment. The variations in Ti^{4+} concentration by doping Mn are summarized in the following. (1) In the undoped component, the Ti^{4+} content is 71.68%, which is lower compared to that in any of the doped components. (2) When the Mn doping level is 0.5 mol%, it effectively suppresses the majority of Ti^{4+} reduction to Ti^{3+} , the proportion of Ti^{4+} increases to 81.95%, consequently resulting in a significant increase in polarization value. (3) At a Mn doping level of 1 mol%, the Ti^{4+} proportion is 81.33%, which is higher than that of the undoped component but slightly lower than the 0.5 mol% Mn-doped component. Compared with the 0.5 mol% Mn doped component, the slight decrease in Ti^{4+} concentration in this component may be associated with a very small amount of Mn ions exceeding the doping limit and beginning to induce the formation of a secondary phase. The onset of the second phase may weaken the impact of Mn doping on the reduction of Ti^{4+} . (4) With an excess Mn doping level of 1.5 mol%, Mn ions not only substitute for Ti^{4+} but also result in Mn surplus, leading to the formation of a significant secondary phase. This secondary phase causes a pronounced decrease in Ti^{4+} content, being reduced to 79.76%, in contrast to the levels observed in the other two doped components.

We have supplemented the relevant statements in the manuscript, as listed in follows:

Notably, the component with a Mn content of 0.5 mol% exhibits the highest proportion of Ti^{4+} content. Further increases in Mn content gradually reduce the Ti^{4+} content but remains higher than that of the undoped component. This variance underscores the impact of the varying Mn concentrations on inhibiting the reduction reaction from Ti^{4+} to Ti^{3+} , where Mn impedes the reduction of Ti^{4+} to Ti^{3+} by reducing its own valence state. At lower Mn doping levels, it effectively suppresses the majority of Ti^{4+} reduction to Ti^{3+} , consequently resulting in a significant increase in polarization value. At higher Mn contents, the slight decrease in Ti^{4+} concentration may be associated with a very small amount of Mn ions exceeding the doping limit and beginning to induce the formation of a secondary phase. The extremely low content of this secondary phase may escape detection by SEM and XRD techniques. The onset of the second phase may weaken the impact of Mn doping on the reduction of Ti^{4+} . Upon excessive Mn doping, besides Mn ions replacing Ti^{4+} , there is a Mn surplus, leading to the formation of a substantial secondary phase that can be detected by SEM and XRD (The characterization and analysis of the secondary phase will be introduced in detail later). The presence of this secondary phase inevitably contributes to the increased polarization loss.

Comment 4: In EPR, authors claim 0.5 mol% Mn doped component shows only one type of signal, corresponding to Mn^{2+} and 1 mol% Mn exhibits both Mn^{2+} and Mn^{4+} signals. It is difficult to distinguish the between the EPR of 0.5% and 1.0% spectrum. How were Mn^{2+} and $4+$ valence states identified in the 1 mol% Mn doped? Could the authors elaborate on the characteristics of this signal and why it is specific to Mn^{2+} in 0.5 mol%?

Author's response:

Thank you very much for your comment. The valence state of Mn ions was determined by analyzing the Electron Paramagnetic Resonance (EPR) spectra of Mn. The EPR spectra of Mn exhibit six characteristic sharp resonance peaks, attributable to the hyperfine splitting of the Mn

isotope with nuclear spin of 5/2 [Journal of Physics and Chemistry of Solids 64, 953-960 (2003); J. Mater. Sci.: Mater. Electron. 30, 2953-2965 (2019)]. The presence of Mn^{2+} or Mn^{4+} can be determined based on whether the signal peaks are split. At doping levels below the maximum doping limit, specifically at 0.5 mol% doping concentration, none of the six signal peaks were split, confirming that Mn exists in its low-valent ionic state. Please check below for detailed information.

For doping concentrations of 0.5 mol% and 1 mol%, the EPR signals of Mn are quite similar. However, as illustrated in the magnified view of the peaks in Figure R6(b) (using the EPR signal peak at lower magnetic fields as an example), a splitting is observed in the EPR signal peaks for 1.0% Mn.

At a lower doping level of 0.5%, without exceeding the doping limit, all Mn exists in low valence states, either +2 or +3, which suppresses the reduction of Ti^{4+} to Ti^{3+} . The presence of Mn^{3+} cannot be confirmed based on the current results, as Mn^{3+} is often referred to as the “EPR-silent” ion due to its negligible zero-field splitting, making its EPR spectrum undetectable at low frequencies in the conventional X-band (~9.5 GHz) [J. Magn. Magn. Mater. 519, 167450 (2021)]. Consequently, only the EPR signal of Mn^{2+} is observed in the NBT-SBT-0.5 mol% Mn sample.

Although the peak positions of Mn^{2+} and Mn^{4+} EPR signals are proximate, there are slight differences, i.e., the EPR signal peaks for Mn^{2+} appearing at lower magnetic fields compared to Mn^{4+} , consistent with reported literature [Journal of Physics and Chemistry of Solids 64, 953-960 (2003); J. Appl. Phys. 104, (2008)]. When the doping concentration is increased to 1 mol%, it is inferred that the doping might exceed the threshold, leading to a small amount of Mn existing in the +4 or +3 states outside the perovskite lattice. Thus, the EPR signals of both Mn^{2+} and Mn^{4+} are observed in the NBT-SBT-1 mol% Mn sample.

We have redrawn the EPR plot of the 1 mol% Mn doped component in *Supplementary Information* Figure S3, and amplified the first signal splitting peak to facilitate readers’ observation of the data. In addition, we have provided a more detailed supplement to the analysis of EPR in the revised manuscript. The updated statements are given below.

The electron paramagnetic resonance (EPR) results are depicted in Figs. 2c and d. The

undoped component did not exhibit any discernible EPR signal for Mn (illustrated by the orange curve in Fig. 2c), whereas the three doped components exhibited six Mn EPR signals (attributable to the hyperfine splitting of the Mn isotope with nuclear spin of 5/2), with signal intensity escalating alongside higher Mn content. Utilizing the component with 0.5 mol% Mn content as an example, it is obvious that there is only one type of signal, i.e., the presence of Mn^{2+} . In contrast, the 1 mol% Mn doped component shows two distinct types of signals: Mn^{2+} and Mn^{4+} . This is evidenced by the observed splitting of the EPR signal peaks in the magnified view of *Supplementary Information Fig. S3*. The Mn^{3+} , often referred to as the “EPR silencing” ion, manifests notable zero-field splitting, rendering its EPR spectrum undetectable at low frequencies in the conventional X-band (~ 9.5 GHz).

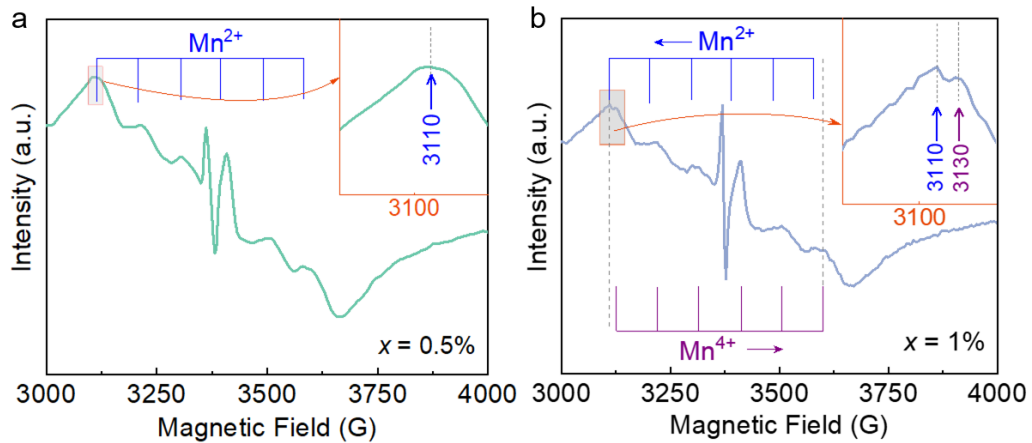


Figure R6. EPR of Mn in (a) NBT-SBT-0.5 mol% Mn and (b) NBT-SBT-1 mol% Mn ceramics.

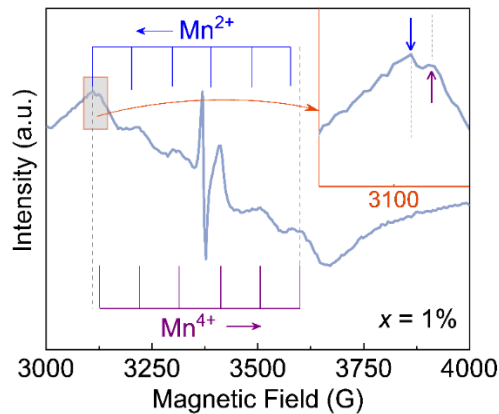


Figure S3 EPR of Mn in NBT-SBT-1 mol% Mn ceramic.

Comment 5: How does the presence of the secondary phase and changes in grain orientation specifically affect the hysteresis and energy storage performance of Mn-doped 0.65NBT-0.35SBT?

Author's response:

Thank you very much for your comment. The presence of the second phase increases the P_r , thereby enhancing the hysteresis of the P - E loops, which leads to a simultaneous decrease in W_{rec} and η . Samples with different grain orientations exhibit slight variations in P_{max} under the same electric field, while the P_r remains nearly unchanged. Due to the minimal electrostriction coefficient Q_{33} along the $\langle 111 \rangle$ direction, $\langle 111 \rangle$ -oriented samples can withstand higher breakdown fields, resulting in higher W_{rec} .

The impact of the secondary phase: The current density-electric field curve presented in *Supplementary Information* Figure S4 demonstrates that excessive Mn doping in NBT-SBT-based ceramics, i.e. doping with 1.5 mol% Mn, leads to a significant broadening of current density peaks due to the formation of a secondary phase, resulting in a pronounced alteration in ferroelectric behavior. Reflected in the hysteresis loop is an increase in hysteresis, with P_r suddenly increasing from $\sim 1.6 \mu\text{C}\cdot\text{cm}^{-2}$ to $5.9 \mu\text{C}\cdot\text{cm}^{-2}$, resulting in a significant increase in hysteresis loss. An increase in the hysteresis of the hysteresis loop signifies a rise in energy loss, which adversely affects the attainment of high energy storage density and efficiency. We hypothesize that the marked increase in hysteresis may be attributed to interface effects between the secondary phase and the ceramic matrix. As depicted in Figure S7, the secondary phase is primarily compressed between the ceramic matrix grains, and the interfaces between the secondary phase and the matrix ceramics might introduce additional polarization effects or impede charge movement, thereby enlarging the hysteresis region of the hysteresis loop. Furthermore, it is acknowledged that the secondary phase could also influence the electrical conductivity. Variations in conductivity can affect the polarization behavior of the ceramic materials under an electric field, thus altering the hysteresis characteristics of the hysteresis loop. Whether the increased hysteresis is due to interface effects or changes in conductivity necessitates more detailed and comprehensive characterization and analysis, which is not the focus of our current work.

Based on the above analysis, the impact of the second phase on ferroelectric properties has been added to the analysis of Figure 3 in the revised manuscript, as follows:

Upon reaching a doping level of 1.5%, the hysteresis becomes larger, and the P_r suddenly increases from $\sim 1.6 \mu\text{C}\cdot\text{cm}^{-2}$ to $5.9 \mu\text{C}\cdot\text{cm}^{-2}$. The current density-electric field curve presented in *Supplementary Information Fig. S4* demonstrates that excessive Mn doping in NBT-SBT-based ceramics leads to a significant broadening of current density peaks due to the formation of a secondary phase, resulting in a pronounced alteration in ferroelectric behavior, that is, the hysteresis loss significantly increases.

The impact of the grain orientation: As illustrated in Figure 5a, there is no significant difference in the hysteresis of the hysteresis loops among samples with the same composition but different grain orientations. Variations in grain orientation only affect the P_{max} , with higher P_{max} being favorable for achieving higher energy storage density. However, the enhancement of energy storage density is also influenced by the breakdown electric field; a higher breakdown electric field correlates with increased energy storage density. Electrostriction is a crucial factor determining the sample's ability to withstand the breakdown electric field. Samples with different grain orientations exhibit varying electrostriction coefficient Q_{33} , with the Q_{33} being largest in the $\langle 001 \rangle$ direction and smallest in the $\langle 111 \rangle$ direction. This implies that samples oriented in the $\langle 111 \rangle$ direction can endure higher breakdown electric fields. Although the P_{max} in the $\langle 111 \rangle$ direction is somewhat reduced, this shortfall is mitigated under high electric fields, resulting in a higher polarization value and, consequently, greater energy storage density for the $\langle 111 \rangle$ -oriented ceramics.

The analysis of Figure 5 in the revised manuscript has also been updated to include the influence of grain orientation on ferroelectric properties and energy storage performance, as follows:

Under $500 \text{ kV}\cdot\text{cm}^{-1}$, the strain is notably high for $\langle 001 \rangle$ -textured MLCCs, reaching 0.79%, followed by nontextured MLCCs at 0.60%, and the lowest for $\langle 111 \rangle$ -textured MLCCs, at only 0.38%. This disparity can be attributed to the lower electrostriction coefficient (Q_{33}) of ABO_3 perovskite crystals in the $\langle 111 \rangle$ direction compared to other directions.

<111>-textured samples achieve the highest W_{rec} , benefiting from both enhanced E_B due to reduced tensile strain and a significant increase in P_{max} induced by a high electric field.

Comment 6: In figure 3d, with the % of Mn doping the dielectric constant increases. What is the reason for this enhancement of dielectric constant?

Author's response:

Thank you very much for your comment. The reason for the increase in dielectric constant of Mn doped components is influenced by the Mn doping concentration. Specifically, (1) the two components with Mn doping contents of 0.5 mol% and 1 mol% prevent Ti^{4+} reducing to Ti^{3+} by lowering their own valence, where the increased concentration of Ti^{4+} enhanced the dielectric constant of the ceramic; (2) At a Mn doping concentration of 1.5 mol%, the formation of a secondary phase induces an abnormal ferroelectric phase transition, leading to an anomalous increase in the dielectric constant. The detailed analysis is listed below.

In Figure 3d, the dielectric constants of the 0.5 mol% and 1 mol% Mn doped components are higher than that of the undoped component. Our experiments and first principles calculations have confirmed that Mn can prevent the reduction of Ti^{4+} to Ti^{3+} in NBT-based ceramics by reducing its own valence, thereby reducing leakage current and increasing P_{max} . The dielectric constant serves as a physical parameter to assess the degree of polarization in a dielectric material. A higher degree of polarization in the material corresponds to a higher dielectric constant. Substituting Mn^{2+} at the B-site increases the off-centering displacements of all ions, leading to greater electric displacement (polarization response) under an electric field and thereby enhancing the polarization of the material. Consequently, the components doped with 0.5 mol% and 1 mol% Mn exhibit a larger dielectric constant.

In addition, the significant increase in dielectric constant near T_2 temperature of the 1.5 mol% Mn doped component is attributed to the excess Mn causing abnormalities in the crystal structure, including the generation of secondary phases.

We have added relevant explanations to the analysis of Figure 3 in the manuscript, as follows:

The dielectric constants of the compositions doped with 5 mol% and 10 mol% Mn are enhanced, due to the doping of Mn preventing the reduction of Ti^{4+} to Ti^{3+} , thereby reducing

the concentration of Ti^{3+} . In contrast, the dielectric constant of the 15 mol% Mn doped composition shows a marked increase near the temperature T_2 , attributed to structural anomalies including the formation of secondary phases induced by the excess Mn.

Comment 7: The Temperature dependent dielectric curve shows broadness and frequency dependent behaviour which is the characteristics of relaxor ferroelectric. The author could calculate the diffusivity parameter to estimate the relaxor nature and relate with the polarization behaviour of samples.

Author's response:

Thank you very much for your comment. We calculated the diffusivity parameter and added corresponding analysis in the revised manuscript.

At 1 MHz, the dielectric relaxation coefficients (γ) for all components fall within the range of 1.85 to 1.98, indicating that the samples are characteristic of typical relaxor ferroelectrics. The hysteresis loops of undoped, 0.5 mol% Mn-doped, and 1 mol% Mn-doped components are very similar in shape and exhibit low hysteresis. In contrast, 1.5 mol% Mn-doped component shows a significantly increased hysteresis in its P - E loop, primarily due to the abnormal ferroelectric phase transition induced by the presence of a secondary phase.

We calculated the γ of Mn doped NBT-SBT samples in the dielectric temperature spectrum, and the calculation results at 1 MHz are shown in the following Figure R7. And we have added the calculation results of the dielectric relaxation coefficient to *Supplementary Information* Figure S5 and supplemented the relevant analysis in the manuscript, as follows:

The dielectric relaxation coefficients (γ) of all components at 1 MHz are between 1.85-1.98, indicating that the samples are characteristic of typical relaxor ferroelectrics. The P - E loops of undoped, 0.5 mol% Mn-doped, and 1 mol% Mn-doped components are very similar in shape and exhibit low hysteresis. In contrast, the markedly increased hysteresis observed in the hysteresis loop of 1.5 mol% Mn-doped component is primarily attributed to the abnormal ferroelectric phase transition induced by the presence of a secondary phase.

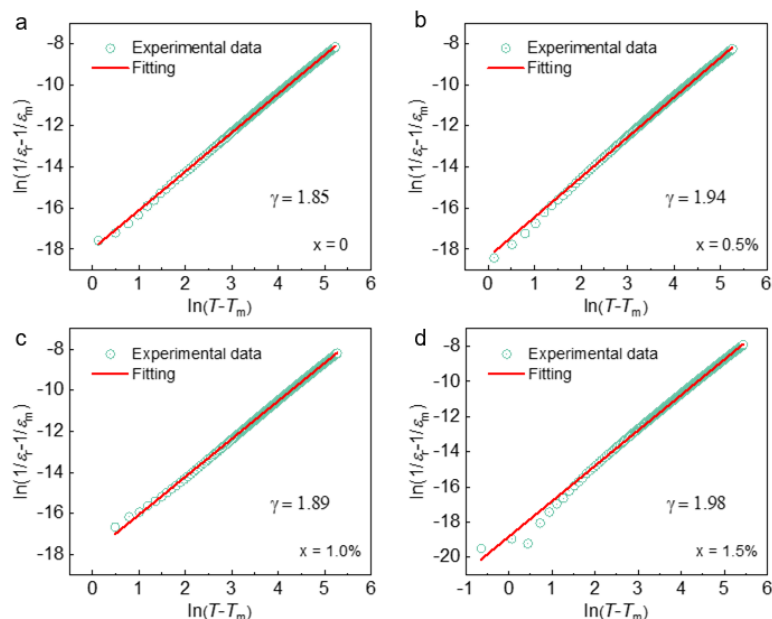


Figure R7. Calculation of dielectric relaxation coefficient of NBT-SBT-xMn ceramics: (a) $x = 0$; (b) $x = 0.5$ mol%; (c) $x = 1.0$ mol%; (d) $x = 1.5$ mol%.

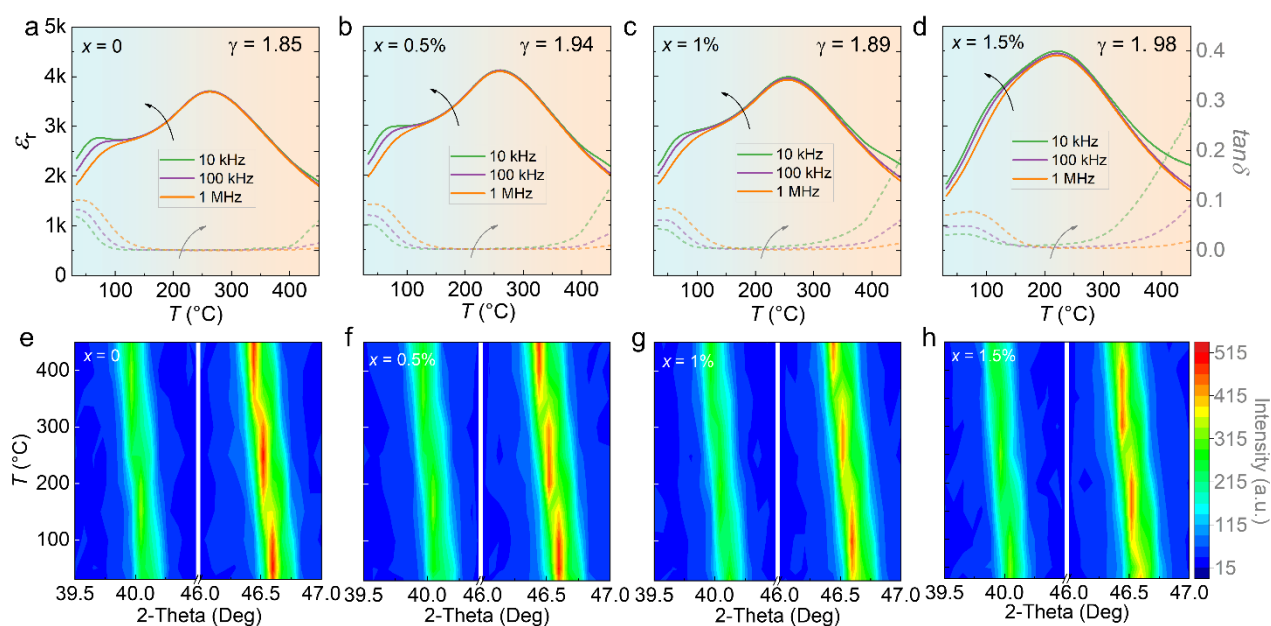


Figure S5 Dielectric temperature spectra and XRD at different temperatures of NBT-SBT-xMn ceramics: (a) $x = 0$; (b) $x = 0.5$ mol%; (c) $x = 1.0$ mol%; (d) $x = 1.5$ mol%.

Comment 8: What is the reason for synthesizing flaky $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ precursor to acquire the $\langle 111 \rangle$ -oriented SrTiO_3 flake microcrystalline template?

Author's response:

Thank you very much for your comment. The reason for synthesizing flaky $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ precursor is that the metastable $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ with monoclinic structure can spontaneously grow in 2D morphology in a molten salt environment. This precursor can then be used to synthesize $\langle 111 \rangle$ -oriented BaTiO_3 flake template through a reasonable topological microcrystal conversion method. Subsequently, the $\langle 111 \rangle$ -oriented SrTiO_3 template can be obtained by substituting Ba^{2+} with Sr^{2+} based on the $\langle 111 \rangle$ -oriented BaTiO_3 template.

We have added the reason for synthesizing flaky $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ precursor to acquire the $\langle 111 \rangle$ -oriented SrTiO_3 flake microcrystalline template in the “Methods” of the manuscript, as follows:

The metastable $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ with monoclinic structure can spontaneously grow in 2D morphology in a molten salt environment, and can be used to synthesize microcrystalline templates with pure perovskite phase through a reasonable topological microcrystal conversion method.

Comment 9: Describe the relationship between the structural variation of $\langle 100 \rangle$ and $\langle 111 \rangle$ and the difference in polarization values between them.

Author’s response:

Thank you very much for your comment. The phase structures of the $\langle 100 \rangle$ -oriented and $\langle 111 \rangle$ -oriented samples are identical, both featuring a minor presence of the tetragonal phase but predominantly composed of the rhombohedral phase. However, in the $\langle 100 \rangle$ -oriented samples, the grains are aligned along the $\langle 100 \rangle$ direction, while in the $\langle 111 \rangle$ -oriented samples, the grains are aligned along the $\langle 111 \rangle$ direction.

The influence of different crystal orientations on polarization is discussed using the rhombohedral perovskite crystal structure as an example. As shown in Figure R8, the polarization direction of the rhombohedral phase is $\langle 111 \rangle$, with eight polarization vectors along the body diagonal: $P_1 [1\bar{1}\bar{1}]$, $P_2 [\bar{1}\bar{1}\bar{1}]$, $P_3 [\bar{1}1\bar{1}]$, $P_4 [11\bar{1}]$, $P_1' [1\bar{1}1]$, $P_2' [\bar{1}\bar{1}1]$, $P_3' [\bar{1}11]$ and $P_4' [111]$. Taking the (110) plane as an example, when no electric field is applied, the polarization vectors on this plane are $P_2 [\bar{1}\bar{1}\bar{1}]$, $P_2' [\bar{1}\bar{1}1]$, $P_4 [11\bar{1}]$ and $P_4' [111]$. Under an applied electric field, $\langle 100 \rangle$ -oriented rhombohedral ceramics exhibit a “4R” engineered domain configuration,

where the polarization reversal process involves 71° and 109° polarization rotations. In contrast, $\langle 111 \rangle$ -oriented rhombohedral ceramics display a single-domain structure, with an ideal polarization reversal involving a 180° rotation. Therefore, compared to $\langle 100 \rangle$ -oriented samples, $\langle 111 \rangle$ -oriented samples are more challenging to polarize, resulting in a delayed saturation polarization.

The relationship between the structural variation of $\langle 100 \rangle$ and $\langle 111 \rangle$ and the difference in polarization values between them were added in the revised manuscript, as follows:

Under an applied electric field, $\langle 001 \rangle$ -oriented rhombohedral ceramics exhibit a “4R” engineered domain configuration, where the polarization reversal process involves 71° and 109° polarization rotations. In contrast, $\langle 111 \rangle$ -oriented rhombohedral ceramics display a single-domain structure, with an ideal polarization reversal involving a 180° rotation. Therefore, compared to $\langle 100 \rangle$ -oriented samples, $\langle 111 \rangle$ -oriented samples are more challenging to polarize, resulting in a delayed saturation polarization.

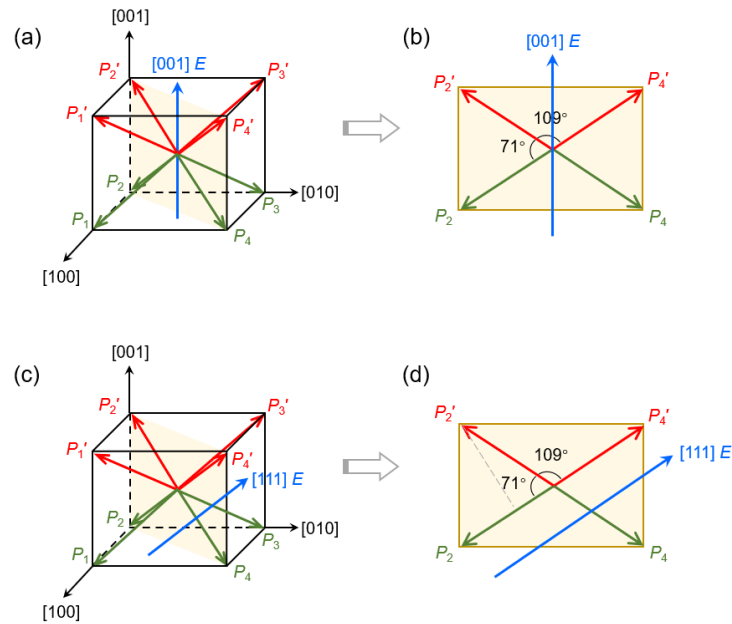


Figure R8. Schematic of the rhombohedral perovskite crystal structure: (a) Crystal structure with $\langle 001 \rangle$ -orientation and the corresponding (b) polarization vectors on the (110) plane; (c) crystal structure with $\langle 111 \rangle$ -orientation and the corresponding (d) polarization vectors on the (110) plane.

Comment 10: Perhaps the authors could have also cite other relevant articles, such as EPR and magnetization studies of the manganites (<https://doi.org/10.1016/j.jmmm.2020.167450>),

<https://doi.org/10.1088/2053-1591/2/9/096301>, and <https://doi.org/10.1063/1.4804940>, DOI 10.1088/1361-6463/aa7fa7, <https://doi.org/10.1063/1.4862169> etc.

Author's response:

Thank you very much for your suggestion. We have thoroughly reviewed the references you provided and have cited them appropriately throughout the manuscript to substantiate our analysis. The newly included references are as follows:

[41] Misra, S., Andronenko, S. I., Padia, P., Vadnala, S. & Asthana, S. EPR and magnetization studies of the manganites $\text{La}_{0.7-x}\text{Eu}_x\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.4, 0.5, 0.6, 0.7$) and $\text{La}_{0.3}\text{Nd}_{0.4}\text{Sr}_{0.3}\text{MnO}_3$ at different temperatures: Conductivity due to hopping of small polarons. *J. Magn. Magn. Mater.* 519, 167450 (2021).

[46] Thangavelu, K. & Asthana, S. Monoclinic Cc -phase stabilization in magnetically diluted lead free $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ —evolution of spin glass like behavior with enhanced ferroelectric and dielectric properties. *Mater. Res. Express* 2, 096301 (2015).

[47] Niranjana, M. K., Karthik, T., Asthana, S., Pan, J. & Waghmare, U. V. Theoretical and experimental investigation of Raman modes, ferroelectric and dielectric properties of relaxor $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *J. Appl. Phys.* 113, 194106 (2013).

[48] Thangavelu, K., Ramadurai, R. & Asthana, S. Evidence for the suppression of intermediate anti-ferroelectric ordering and observation of hardening mechanism in $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ ceramics through cobalt substitution. *AIP Adv.* 4, 017111 (2014).

Thank you again very much for your careful reading and scientific comments concerning our manuscript. Please kindly let us know if you need any further information.

Sincerely Yours,

Fei Li & Shujun Zhang, on behalf of all co-authors.

REVIEWERS' COMMENTS

Reviewer #1:

The authors have provided thorough and meaningful responses to the reviewers' comments and have revised the manuscript accordingly. Therefore, the paper is deemed suitable for publication.

Authors' response: Thank you very much for reviewing our revised manuscript and we appreciate your positive comment.

Reviewer #3:

The main point raised in the review report was that "Why DFPT calculation was not carried out on a composition close to that of experimental composition?". Authors have pointed out that the DFPT calculation was carried out on $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ as it is major component (65%) and also due to the computational challenge involved in terms of reasonably large super cell to match the experimental composition. Further, the computational result is that Mn^{2+} substitution improves the polarisation. This result was compared only qualitatively to the selected experimental composition. Authors reply may be considered positively.

Authors' response: Thank you very much for reviewing our revised manuscript. We appreciate your understanding of the challenges involved in this aspect of the work and your positive comment.

Reviewer #4:

Authors have addressed the comments in details. It can be accepted.

Authors' response: Thank you very much for reviewing our revised manuscript and we appreciate your positive comment.