

Global-optimized energy storage performance in multilayer ferroelectric ceramic capacitors

Corresponding Author: Professor Di Zhou

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 work shows a high performance and thermally stable lead-free MLCC made of ternary ceramic, which is very detailed and promising. However, there is a similar work published earlier [X. Xiong, et al, Ultrahigh Energy-Storage in Dual-Phase Relaxor Ferroelectric Ceramics. Adv. Mater. 2024, 2410088] which is also lead-free ternary relaxor ferroelectric ceramic containing mixed phases and showing higher energy storage density and efficiency at room temperature and comparable properties at 180 °C. So, this work may lack sufficient novelty to be considered for publication in Nature Communications.

In figure 2, there is impurity peak at ~28 deg. in XRD patterns of all the four samples. The authors described the grain size as uniform and normal, however, it is obvious from the histogram that the grain size of sample 65-20-15 and 60-20-20 are not uniform.

In Figure 1c, the phase field simulation shows higher ST corresponds to higher W_{rec} , however, the experimental result in Figure 3d shows a reverse tendency.

Reviewer #2

(Remarks to the Author)

The manuscript by Li et al., titled "Global-optimized energy storage performance in multilayer ferroelectric ceramic capacitors," reports a notable energy density (W_{rec}) of 20.0 J·cm⁻³, coupled with a high efficiency (η) of 86.5% and remarkable high-temperature stability in ferroelectric ceramic capacitors, which is quite interesting. I have the following suggestions for the authors to consider:

1. The authors state that the capacitors are MLCCs. However, how did they verify that the prepared capacitors are MLCCs and not composite capacitors? Please clarify.
2. The authors prepared various samples of (1-x)BNT-0.20NN-xST (x = 0.15, 0.20, 0.25, and 0.30) and (55-20-25-Mn). It is unclear whether only the last sample is an MLCC or if all samples are intended to be MLCCs. Please justify.
3. Is there a specific reason for selecting 1% mol of MnO₂, and why MnO₂ was chosen over other dopants? Additionally, it would be helpful to include the XRD analysis for this sample.
4. Please provide details on the area and thickness of the MLCC.
5. While the energy density of the MLCCs is higher than that of typical ferroelectric ceramic capacitors, thin-film capacitors generally exhibit even higher energy densities. Please reconsider or revisit the use of the term "ultra" to ensure the message is accurate for a broader audience.

Reviewer #3

(Remarks to the Author)

Reviewer comments to authors:

Obtaining high energy density ($W_{rec} \geq 15 \text{ J cm}^{-3}$) and minimal losses ($\eta \geq 90\%$) simultaneously is a persistent objective for all researchers. The trade-off between W_{rec} and η is a key challenge in designing high-performance dielectric ceramics. The authors have done a commendable work to overcome these challenges.

Noteworthy results:

In this study, W_{rec} of $\sim 20.0 \text{ J cm}^{-3}$ and a high η of 86.5% with high cyclic reliability (~ 104 cycles) is reported for $(1-x)\text{BNT}-0.20\text{NN}-x\text{ST}$ MLCC samples with $x=0.25$ by the authors. The authors ascribe these results to domain wall engineering and polymorphic polarization configuration in the multiphase solid solutions. The dielectric response is identical to relaxors and hence low switching energies are obtained. Additionally, the energy storage characteristics show robust frequency and temperature stability along with excellent charge-discharge characteristics.

Methodology and data interpretation:

The authors have systematically studied BNT-NN-ST ternary system to obtain optimum results.

They have used complimentary techniques to predict and obtain reproducible data. They first simulated the phase-field maps to determine the compositions for best theoretical parameters. Then they have synthesized high quality ceramics and MLCC samples.

Further, they have measured the various physical parameters for both ceramics and MLCC. They were able to demonstrate that by making MLCC samples, it is possible to manipulate and control configurational entropy, polarization coupling effects, grain size etc. to obtain results which are superior to the parent ceramic samples. The authors have made a sound interpretation of the data and drawn appropriate conclusions. The study is exhaustive and provides all information to reproduce the work. While there is always a scope for improvement, however the work is suitable for publication with a few minor corrections.

Minor corrections:

Structure determination: While STEM data is helpful in determining local symmetry, to establish the coexistence of multiple phases unambiguously globally, Rietveld refinement data for 4 compositions should be added in the supplementary information to quantify each phase. This information will help in appreciating how the different phase fractions can be used to tailor ferroelectric properties.

Leakage current and correlation with grain size: In the discussion, it is asserted that grain refinement due to ST doping can enhance the E_b and reduce the leakage current, which is conducive to energy storage. To establish this, leakage current studies at room temperature for 4 compositions under 900 kV/cm need to be shown in supplementary data.

Supplementary data_fig.S3: Why is the temperature dependent dielectric behavior for $x=0.30$, especially the dielectric loss, so different from other compositions? Any explanations?

Recommendation:

This is a significant work and I recommend publication of this article with aforementioned minor corrections.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors has addressed all the questions and it is good to be accepted.

Reviewer #2

(Remarks to the Author)

The manuscript has been thoroughly revised, with all reviewer comments addressed and improvements made to enhance clarity, data presentation, and scientific rigor. Each section was refined to align with publication standards, resulting in a polished, well-supported version.

Reviewer #3

(Remarks to the Author)

I am satisfied with the authors responses to all the queries raised. The manuscript is now ready for publication in the revised form and I recommend to publish it.

Rajesh Katoch

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Responses to Reviewer # 1:

Reviewer #1 (Remarks to the Author):

Comments 1: This work shows a high performance and thermally stable lead-free MLCC made of ternary ceramic, which is very detailed and promising. However, there is a similar work published earlier [X. Xiong, et al, Ultrahigh Energy-Storage in Dual-Phase Relaxor Ferroelectric Ceramics. Adv. Mater. 2024, 2410088] which is also lead-free ternary relaxor ferroelectric ceramic containing mixed phases and showing higher energy storage density and efficiency at room temperature and comparable properties at 180 °C. So, this work may lack sufficient novelty to be considered for publication in *Nature Communications*.

Responses: We appreciate the reviewer's comment. With the fast developments of energy requirements, energy storage capacitors have attracted much attention in recent years and novel results are continuously reported in high-reputation journals. X. Xiong, et al. reported novel relaxor ferroelectric ceramics for energy storage applications, which was published in Advanced Materials. Both Xiong's and our works involve the optimization of the energy storage performance of ternary relaxor ferroelectric ceramics with multiphase coexistence structures. Nevertheless, there are also significant differences between them, mainly including the following:

(1) **Different research objects:** In our work, it not only encompasses the preparations and performance research of bulk ceramics but, more significantly, we have fabricated MLCC (Multilayer Ceramic Capacitors) prototype devices by employing advanced processes like tape casting and screen printing. Additionally, we

have analyzed the impact of adding sintering additives on the phase, dielectric, and ferroelectric properties of ceramics and resolved the co-firing issue of metal electrodes and ceramic dielectrics. This offers a new perspective for the traditional MLCC manufacturing industry to address such problems, which is not covered in the work you pointed out.

(2) **Different research schemes:** We first optimized the possible best composition by simulating the *P-E* loops of the $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-NaNbO}_3\text{-SrTiO}_3$ (BNT-NN-ST) system in the entire composition range. The experimental research is guided by the phase field simulation results. The research schemes of the two are entirely different.

(3) **Different technical approaches:** For instance, we employed a mesoscale simulation method to investigate the evolution of the polar structure of materials. Xiong et al. utilized the phase field method to simulate the breakdown behavior of ceramics. Clearly, the technical means of the two are distinct.

(4) **Different design strategies:** Xiong et al. adopted the strategy of constructing dual perovskite phase RFE ceramics through in situ phase separation. In our work, it is a combination of constructing local polymorphic polarization configuration and manufacturing prototype devices. The design strategies of the two are completely different.

Comments 2: In figure 2, there is impurity peak at $\sim 28^\circ$ in XRD patterns of all the four samples. The authors described the grain size as uniform and normal, however, it is obvious from the histogram that the grain size of sample 65-20-15 and 60-20-20 are not uniform.

Response: We know that for XRD testing, the test results are influenced by the precision of the instrument and parameter settings, including the voltage and current values of the X-ray tube, slit size, and scanning speed. To avoid contingency, we utilized another X-ray diffraction analyzer (D8 Advance, Bruker, Germany) to record the XRD patterns of all the four ceramic samples, as shown in Fig. 1. We discovered that all the ceramics possess high-quality crystallinity and a single perovskite structure. Furthermore, we adjusted both the scanning speed of 1° min^{-1} and the 2θ range of 10° - 120° to test the 55-20-25 ceramic, as depicted in Fig. 2. All the results demonstrate that the ceramic samples we prepared possess a single perovskite structure and no second phase is generated.

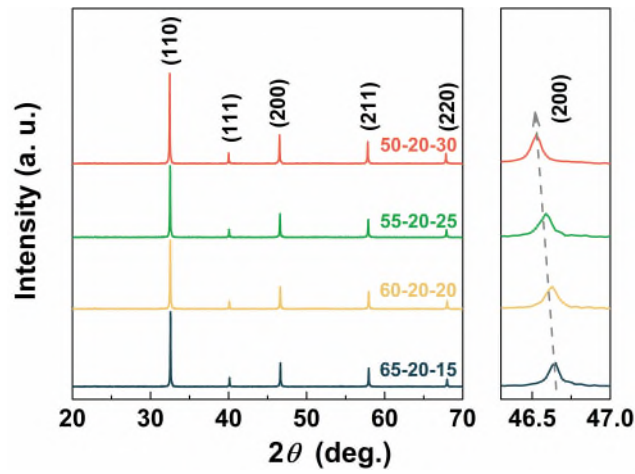


Fig. 1 XRD patterns of $(1-x)\text{BNT}-0.20\text{NN}-x\text{ST}$ ceramics.

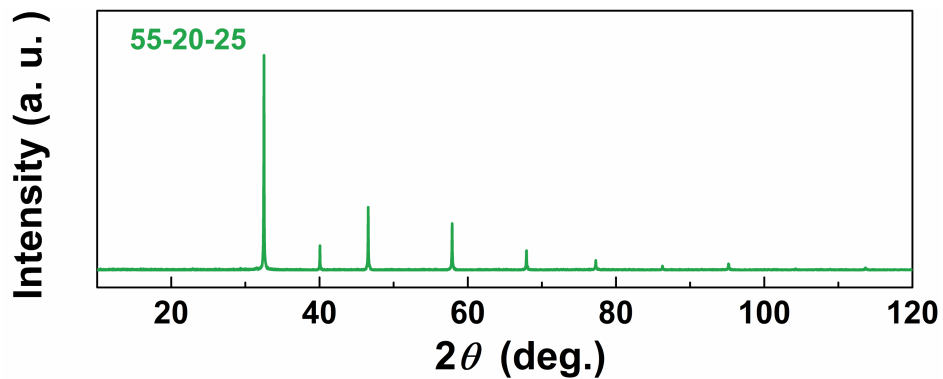


Fig. 2 XRD patterns of 55-20-25 ceramics.

As observed from Fig. 3 (Original Fig. 2e), it seems that the particle size distributions of the 65-20-15 and 60-20-20 samples are not uniform. However, in fact, as seen from the fitting curve in the histogram, it is in line with a normal distribution. Moreover, for the 65-20-15 and 60-20-20 ceramics, grains with smaller sizes account for a relatively large proportion, which is beneficial for the ceramics to achieve a higher breakdown strength.

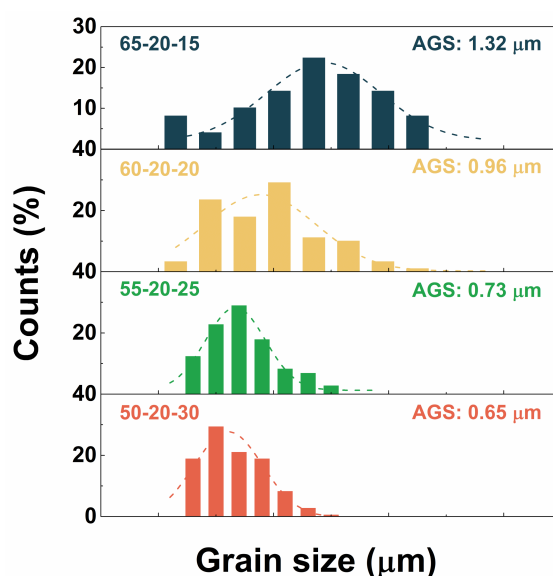


Fig. 3 (Original Fig. 2e) Grain size distribution of ceramics.

Comments 3: In Figure 1c, the phase field simulation shows higher ST corresponds to higher W_{rec} , however, the experimental result in Figure 3d shows a reverse tendency.

Response: In fact, the Original Fig. 1c describes contour plots of the simulated η of BNT-NN-ST solid solutions, as shown in Fig. 4a below. The simulation results show that compositions with more ST content exhibit higher η . It is normal for there to be differences between theoretical simulations and experimental results. In experimental testing, there are many factors that affect the macroscopic performance parameters of samples, such as the thickness of the sample, the sputtering quality of the electrode, the

porosity of the sample, and so on. The “reverse tendency” mentioned by the reviewer is only that the energy efficiency (91.0%) of the 50-20-30 ceramic is not greater than that of the 55-20-25 ceramic (93.1%), and this slight gap is common in mathematical simulations. In addition, the highest W_{rec} is located inside the triangle (Fig. 4b, Original Fig. 1d), which implies that the energy storage potential of the one-component or binary system is lower than that of the BNT-NN-ST ternary solid solution, which is consistent with the experimental results (Fig. 4c, Original Fig. 3d).

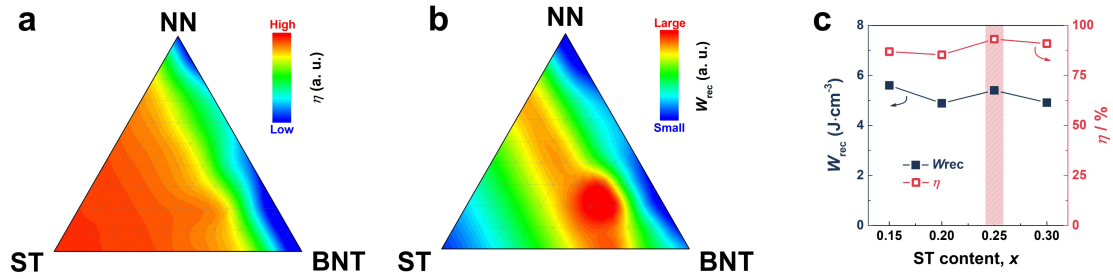


Fig. 4 Contour plots of the simulated **a** (Original Fig. 1c) η and **b** (Original Fig. 1d) W_{rec} of BNT-NN-ST solid solutions. **c** (Original Fig. 3d), W_{rec} and η for (1- x)BNT-0.20NN- x ST ceramics.

Responses to Reviewer # 2:

Reviewer #2 (Remarks to the Author):

The manuscript by Li et al., titled "Global-optimized energy storage performance in multilayer ferroelectric ceramic capacitors," reports a notable energy density (W_{rec}) of $20.0 \text{ J}\cdot\text{cm}^{-3}$, coupled with a high efficiency (η) of 86.5% and remarkable high-temperature stability in ferroelectric ceramic capacitors, which is quite interesting. I have the following suggestions for the authors to consider:

Comments 1: The authors state that the capacitors are MLCCs. However, how did they verify that the prepared capacitors are MLCCs and not composite capacitors? Please clarify.

Response: Thank you for your comment. There exist numerous types of capacitors, among which are composite capacitors and multilayer ceramic capacitors. Composite capacitors are typically made of metallized composite film dielectric and are suitable for direct current or pulsating circuits. The research object in our work is a multilayer ceramic capacitor. It is formed by stacking ceramic dielectric films printed with electrodes in a staggered fashion and then sintering at a high temperature. It is applicable in scenarios such as filtering and tuning. As can be observed from the provided cross-sectional microstructures and element distribution map (Fig. 5, Original Fig. 4a), the capacitor prepared in this work is indeed made from ceramic powders that is formed into ceramic films by tape casting rather than metallized composite films. Subsequently, after screen printing the internal electrodes, the layers are stacked in a staggered manner. Finally, it is fabricated through processes such as hot pressing, debinding, and sintering. These descriptions can be found in the Methods section, and

the Methods section has been moved from the Supplementary Information to the main text.

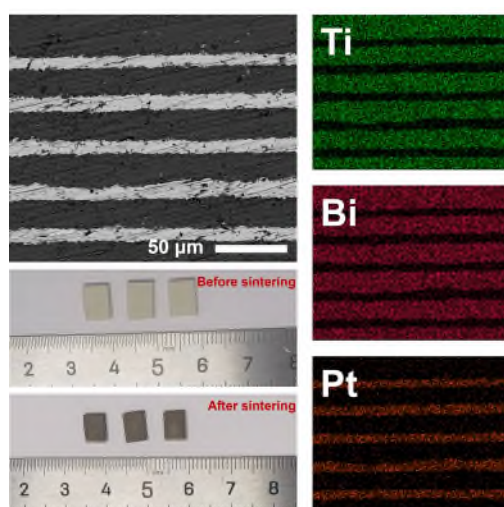


Fig. 5 (Original Fig. 4a) Digital images of the MLCCs and SEM images of the cross-section area with corresponding element distribution.

Comments 2: The authors prepared various samples of $(1-x)\text{BNT}-0.20\text{NN}-x\text{ST}$ ($x=0.15, 0.20, 0.25$, and 0.30) and $(55-20-25-\text{Mn})$. It is unclear whether only the last sample is an MLCC or if all samples are intended to be MLCCs. Please justify.

Response: We apologize for any confusion. The research route of this work is as follows. Firstly, the possible optimal composition is selected by simulating the P - E loops of the BNT-NN-ST system in the entire composition range, that is, $(1-x)\text{BNT}-0.20\text{NN}-x\text{ST}$ ($x=0.15, 0.20, 0.25$, and 0.30). Then, bulk ceramics are prepared according to the formula composition, and the various physical properties of these ceramic samples, including energy storage performance, are studied. Based on the obtained results, the ceramic powder with the most appropriate comprehensive performance (55-20-25 composition) is selected to prepare MLCC. However, in order to better solve the shrinkage matching problem between the internal electrode and the dielectric during

co-firing, MnO_2 is added as a sintering aid and 55-20-25-Mn ceramics are prepared. Subsequently, we conducted a systematic study on the phase, microstructure, element distribution, energy storage performance, and mesoscale phase field simulation of the 55-20-25-Mn ceramics. Finally, we selected the 55-20-25-Mn powder and used a series of advanced processes to prepare the 55-20-25-Mn MLCC sample. To make the article more organized, explanations about the samples have been added in multiple locations in the text. For details, please see the highlighted parts of the revised manuscript.

Comments 3: Is there a specific reason for selecting 1% mol of MnO_2 , and why MnO_2 was chosen over other dopants? Additionally, it would be helpful to include the XRD analysis for this sample.

Response: The selection of the sintering aid MnO_2 is based on extensive literature review. Numerous studies have demonstrated that the addition of a small amount of MnO_2 can effectively reduce the porosity of ceramics, lower the sintering temperature, decrease the shrinkage rate during sintering, and reduce the Curie temperature¹⁻⁴. In this work, 1.0% mol MnO_2 is added to the 55-20-25 ceramic as a sintering aid (abbreviated as 55-20-25-Mn). This is done to reduce the sintering temperature of MLCC and optimize the shrinkage matching degree between the dielectric and the internal electrode. Additionally, XRD pattern of the 55-20-25-Mn ceramic is provided in Fig. 6 (Original Fig. S7). XRD results indicate that the introduction of MnO_2 does not alter the crystallographic structure, only slight shift to a lower angle of the diffraction peaks of the MnO_2 -doped ceramic.

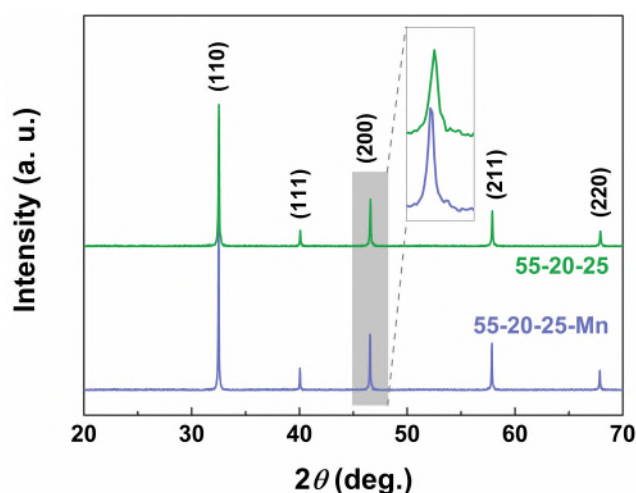


Fig. 6 (Original Fig. S7) XRD patterns of 55-20-25 and 55-20-25-Mn ceramics.

The references are as follows:

- [1] Quan, Y. *et al.* Effects of MnO₂ addition on the electrical properties of lead-free textured potassium sodium niobate-based ceramics. *Ferroelectrics* **553**, 51-59, (2020).
- [2] Tipakontitikul, R. *et al.* Effects of MnO₂ addition on the dielectric behaviors of the PZT-PMN ceramics. *Ferroelectrics* **381**, 144-151, (2009).
- [3] Park, M. *et al.* Piezoelectric and dielectric properties of nonstoichiometric (Na_{0.5}K_{0.5})_{0.97}(Nb_{0.90}Ta_{0.1})O₃ ceramics doped with MnO₂. *J. Electron. Mater.* **41**, 3095-3099 (2012).
- [4] Lin, D. *et al.* Dielectric and piezoelectric properties of MnO₂-doped K_{0.5}Na_{0.5}Nb_{0.92}Sb_{0.08}O₃ lead-free ceramics. *J. Mater. Sci.: Materi. El.* **21**, 649-655, (2009).

Comments 4: Please provide details on the area and thickness of the MLCC.

Response: Thank you for your valuable suggestion. The overlapping area of two adjacent platinum electrodes in the sintered MLCC is measured to be 2.1 mm × 1.6 mm,

and the average thickness is approximately 20 μm , as depicted in Fig. 7. This has been added to the MLCCs fabrication section in the revised manuscript.

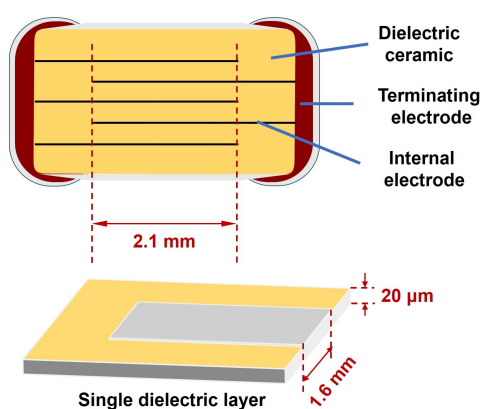


Fig. 7 Structure diagram of MLCC.

Comments 5: While the energy density of the MLCCs is higher than that of typical ferroelectric ceramic capacitors, thin-film capacitors generally exhibit even higher energy densities. Please reconsider or revisit the use of the term "ultra" to ensure the message is accurate for a broader audience.

Response: To ensure the accuracy of the information for a wide audience, we have thoroughly checked the entire text and revised extreme words such as “ultra” and “extremely”. For details, please see the highlighted parts of the revised manuscript.

Responses to Reviewer # 3:

Reviewer #3 (Remarks to the Author):

Reviewer comments to authors: Obtaining high energy density ($W_{\text{rec}} \geq 15 \text{ J cm}^{-3}$) and minimal losses ($\eta \geq 90\%$) simultaneously is a persistent objective for all researchers. The trade-off between W_{rec} and η is a key challenge in designing high-performance dielectric ceramics. The authors have done a commendable work to overcome these challenges.

Noteworthy results: In this study, W_{rec} of $\sim 20.0 \text{ J} \cdot \text{cm}^{-3}$ and a high η of 86.5% with high cyclic reliability ($\sim 10^4$ cycles) is reported for (1-x)BNT-0.20NN-xST MLCC samples with $x=0.25$ by the authors. The authors ascribe these results to domain wall engineering and polymorphic polarization configuration in the multiphase solid solutions. The dielectric response is identical to relaxors and hence low switching energies are obtained. Additionally, the energy storage characteristics show robust frequency and temperature stability along with excellent charge-discharge characteristics.

Methodology and data interpretation: The authors have systematically studied BNT-NN-ST ternary system to obtain optimum results. They have used complimentary techniques to predict and obtain reproducible data. They first simulated the phase-field maps to determine the compositions for best theoretical parameters. Then they have synthesized high quality ceramics and MLCC samples. Further, they have measured the various physical parameters for both ceramics and MLCC. They were able to demonstrate that by making MLCC samples, it is possible to manipulate and control

configurational entropy, polarization coupling effects, grain size etc. to obtain results which are superior to the parent ceramic samples. The authors have made a sound interpretation of the data and drawn appropriate conclusions. The study is exhaustive and provides all information to reproduce the work. While there is always a scope for improvement, however the work is suitable for publication with a few minor corrections.

Response: We greatly appreciate the referee for her/his time to review our manuscript and give us the above extremely encouraging comments. The enlightening suggestions are very helpful for improving this work. Thus, we have revised our manuscript accordingly.

Minor corrections:

Comments 1: Structure determination: While STEM data is helpful in determining local symmetry, to establish the coexistence of multiple phases unambiguously globally, Rietveld refinement data for 4 compositions should be added in the supplementary information to quantify each phase. This information will help in appreciating how the different phase fractions can be used to tailor ferroelectric properties.

Response: This is a fundamental question in perovskite oxides. For example, in BaTiO₃, temperature variations can lead to the observation of cubic (*C*), tetragonal (*T*), orthorhombic (*O*), and rhombohedral (*R*) phases. The characterization of these phases primarily relies on determining the arrangement of BO₆ (TiO₆ in BaTiO₃) octahedra within the structure, specifically the positions of oxygen atoms. Powder diffraction patterns at *M*-points (comprising two odd numbers and one even number Miller indices), *R*-points (with three odd numbers Miller indices, particularly 111), and *X*-points

(involving one odd number and two even numbers Miller indices) enable the determination of the actual phase in perovskite oxides. Normally, the intensity distribution of the peaks in PXRD by the Rietveld refinement gives some information of the phase proportion. However, peaks at superlattice-index positions are typically weak, especially for laboratory X-ray diffraction. The *C*, *T*, *O*, *R* phases are possible at short range order. However, **X-ray diffraction (XRD) is based on long-range ordered crystal structures. The symmetry of the phases limits the distinguishing of the phases where *C* phase has the reflections marks included by *T* phase and *O* by *R*.** Therefore, although the XRD refinement data of the 55-20-25 ceramics have been collected (as shown in Fig. 8), it is not feasible to calculate the percentage of all the four phases by using laboratory PXRD data.

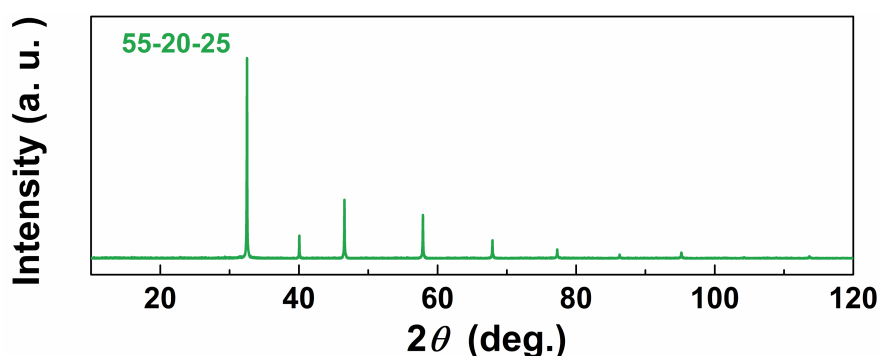


Fig. 8 XRD patterns of 55-20-25 ceramics.

Comments 2: Leakage current and correlation with grain size: In the discussion, it is asserted that grain refinement due to ST doping can enhance the Eb and reduce the leakage current, which is conducive to energy storage. To establish this, leakage current studies at room temperature for 4 compositions under 900 kV/cm need to be shown in supplementary data.

Response: As you suggested, we have supplemented the test of the leakage current

density of four compositions (as shown in revised Fig. 9). The setting of the applied electric field refers to previous work (approximately $100 \text{ kV} \cdot \text{cm}^{-1}$)¹. The results confirm that the leakage current density gradually decreases with the increase of ST content, which confirms the viewpoints stated in our manuscript. The figure has been added to the Supplementary Information file and the relevant discussions have been added to the highlighted parts in the text.

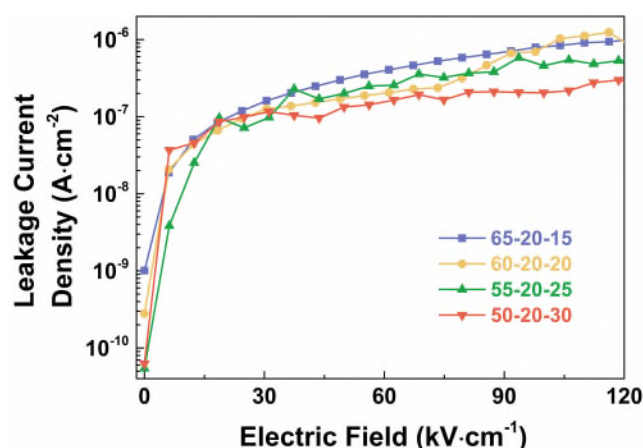


Fig. 9 Leakage current densities as a function of electric field of $(1-x)\text{BNT}-0.20\text{NN}-x\text{ST}$ ceramics.

The references are as follows:

- [1] Zhang, M. et al. Ultrahigh energy storage in high-entropy ceramic capacitors with polymorphic relaxor phase. *Science* **384**, 185-189 (2024).

Comments 3: Supplementary data_Fig.S3: Why is the temperature dependent dielectric behavior for $x=0.30$, especially the dielectric loss, so different from other compositions? Any explanations?

Response: There are many factors that affect the dielectric properties of ceramics, such as the thickness and the sintering temperature of the sample, the sintering quality of the electrodes, and the surrounding environment of the testing equipment. To avoid

contingency, we retested the dielectric properties of the 50-20-30 sample, as shown in Fig. 10. Its dielectric loss at room temperature is less than 0.05, and the dielectric constant exhibits a good frequency dispersion characteristic. For the entire BNT-NN-ST system, the T_m value also gradually shifts towards room temperature as the ST content increases.

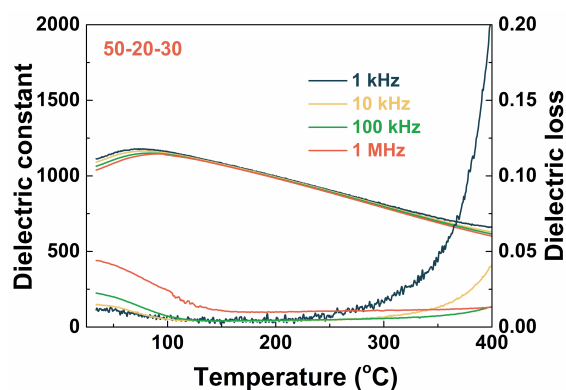


Fig. 10 Temperature-dependent dielectric constant and dielectric loss of 50-20-30 ceramic.

Comments 4: This is a significant work and I recommend publication of this article with aforementioned minor corrections.

Response: Thank you so much for your recognition and we have provided a point-by-point response to your valuable comments and look forward to your approval.