

Advanced stability and energy storage capacity in hierarchically engineered Bi_{0.5}Na_{0.5}TiO₃-based multilayer 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 manuscript reported the energy storage performance of MLCC with ultrahigh energy density and efficiency. For the real application of energy storage capacitor, real total amount of stored energy and applied voltage are more important than the energy density and electric field. In this regard, MLCC with thick film is very useful for real applications. If authors provide the total energy(J) and real applied voltage and emphasize the advantage of MLCC, then these information will be very useful for commercialization.

BKNT + SST to modify the chemical composition. Whis is the reason to select the SST for example, similar atomic size and ferro/antiferro phase? It is strongly recommended to state the reason in more detail.

As the amount of SST increases, BKNT turned from FE to AFE to paraelectrics. Is it right? If authors provide the supporting data for this transition, that will be useful for other researchers to develop the higher energy density capacitors.

In the experimental, authors mentioned 'pre-sintered powders'. What is the state of pre-sintered powders? Is it the calcined powder?

Did you mix the polymer and ceramic powder altogether using high energy mill for 3 hours?

The resultant MLCC green bodies were calcined at 360 °C for 8 hours: calcined?

Following deblending, : what does deblending mean?

For one hour for 1 hour

Per min ? min⁻¹ : please unify the description of dimension.

Authors should revise the MLCC fabrication process using the common nomenclature.

Is this following procedure right?

Tape casting Green body Warm isostatic pressing burn-out the organic CIP HIP silver pasting on both sides of the MLCC

This process is not common for MLCC. Why did not you make the Pt electrodes in the beginning?

How did you connect each electrode in the layer?

Are the fig (data) from MLCC sample or bulk sample? The process for bulk sample and MLCC is different each other, then the microstructure is also different resulting to the different properties.

In the fig. 1, authors draw the polar region with small arrow. Is this a domain? Then what is the grain? IF there were no grain, then sample should not show XRD pattern like glass.

To support the small polar region (small arrow in Fig. 1c), authors should indicate the region in the TEM image.

Reviewer #2

(Remarks to the Author)

Evaluation Report

The authors implemented a polar glass state (PGS) strategy to enhance the energy storage performance of BNT-based multilayer ceramic capacitors (MLCCs) by modulating dynamic and thermodynamic processes. This approach reduced hysteresis loss, improved breakdown strength, and optimized nano-domain disruption and grain refinement through hierarchical structural engineering. As a result, the capacitors achieved an ultra-high recoverable energy density (W_{rec}) of 22.92 J/cm³ and an exceptional efficiency (η) of 97.1%, along with superior high-temperature stability. The proposed strategy provides a transformative blueprint for developing next-generation dielectric capacitors for high-temperature applications. Below are some comments which should be addressed properly before resubmission.

1. Does the proposed polar glass state (PGS) strategy sufficiently explain the enhancement observed in energy storage performance? Are there alternative mechanisms that could contribute to the improved breakdown strength and reduced hysteresis loss? Need further discussion. Refine introduction portion. Few other refs may be useful in refining introduction and cite them at appropriate places.

<https://doi.org/10.1016/j.jallcom.2017.10.126>

10.1088/1361-6463/aa7fa7

<https://doi.org/10.1016/j.jmat.2021.12.007>

<https://doi.org/10.1016/j.matlet.2021.130577>

<https://doi.org/10.1063/1.5021410>

10.1088/1361-6463/aaada1

2. There are many works in MLCCs which have prominent results as compared to the present data. The author needs to explore more and comparative discussion should be provided.

3. Free energy curve is not needed to discuss elaborately. I felt disconnected

4. Why 1.88R-MLCCs have porosity and provide thermal itching Surface morphology?

5. Describe the relationship between the structural variation and the difference in polarization values between them.

6. How does the hierarchical structural engineering approach specifically influence the nano-domain disruption and grain refinement? Try high-resolution microscopy or in-situ techniques provide further insights into these structural modifications.

7. The study claims state-of-the-art high-temperature stability. What are the precise operational temperature limits of the MLCCs, and how do they compare them with commercially available dielectric capacitors in terms of energy density and efficiency at elevated temperatures?

8. How feasible is the large-scale fabrication of BNT-based MLCCs with the PGS strategy? What are the key processing challenges, and how do they impact the reproducibility and manufacturing cost of these capacitors?

9. While the work demonstrates excellent performance metrics, have accelerated lifetime tests (such as fatigue, thermal cycling, or humidity resistance) been conducted to assess the long-term reliability of these MLCCs under real-world operating conditions?

10. Cite some of the recent publications in energy storage paper.

(<https://doi.org/10.1016/j.jallcom.2022.167340>, <https://doi.org/10.1016/j.est.2024.112020>,

<https://doi.org/10.1016/j.mseb.2023.117038>, <https://doi.org/10.1016/j.jallcom.2024.17827>)

Reviewer #3

(Remarks to the Author)

The manuscript studies the energy storage properties of sodium bismuth titanate (NBT)-based multilayer capacitors. Due to a poor description of the methodology, it is impossible to reproduce any of the formulations in either bulk or multilayer form, as well as some of the experiments. The insufficient quality of the data makes the conclusions of this paper unreliable.

The strategy to achieve the polar glass state, as explained on p. 6 is to control the chemical heterogeneity and to balance between thermodynamics and kinetics ('dynamics') upon sintering. While chemical heterogeneity is achieved by inserting four A-site and three B-site cations with different charges into the perovskite lattice, it is not explained how thermodynamics and kinetics are controlled or balanced upon sintering. It is written on the same page that the polar glass state is achieved by the sintering conditions (T and t). However, this is not later developed in the results section. Then, on p. 7, it is written that as opposed to polar nanoregions, atomic scale polarisation is achieved in the study. It is not evident how and why ferroelectric and antiferroelectric interactions arise. In brief, the strategy described at the beginning of the results section is not convincingly confirmed in later parts.

When discussing energy storage, the breakdown field plays a significant role. It is known from the literature that the dielectric breakdown field (or strength) is inversely proportional to several material parameters. It decreases with increasing element thickness, grain size, presence of secondary phases, porosity (fraction and pore size), electrode size, temperature and so on. It is thus not evident what the purpose of comparing the samples prepared by different routes is or, in other words, why show the radar graph in Figure 2c. Presumably, the samples had different thermal budgets, which are not specified well enough. It is worth noting that the sintering temperatures and times are given as temperature ranges, such as 1030 – 1150 °C for MLCCs. The samples had different microstructures, and they behaved differently in terms of their energy storage properties. It is worth noting that the microstructures should be prepared following conventional metallographic procedure, i.e., polishing and etching.

It would be necessary to include the dielectric permittivity data (real and imaginary parts) in broader temperature and frequency ranges. Similarly, it would be helpful to measure the P-E loops also at lower temperatures. Figure S4 does not provide enough data for a reliable assessment of the nature of the studied materials.

The comparison with the literature as shown in Figure 2 f should include exact references. Providing them on-site should be the responsibility of the authors and not left to the reader to pinpoint which of the references cited in the text corresponds to a given dataset.

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors revised the manuscript, but it is not in a better shape for readers to understand their work more clearly. However, there are still some critical issues that need to be resolved before the final decision.

1. It seems that the title does not convey the information on their detail experimental results.
2. The energy storage performance is strongly dependent on the density. What is the density of MLCC And bulk sample for different experimental conditions, such as different calcined temperature and sintering temperatures?

Reviewer #2

(Remarks to the Author)

Authors have done extensive work to resolve the doubts. It can be accepted

Reviewer #3

(Remarks to the Author)

The responses of the authors and the revised manuscript provide explanations to some critical point raised in the review of the original version.

There are no further comments-

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Authors resolved the issues from reviewer.

Small comments: 2 hours, 1h

It is better to unify the words.

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Responses to Reviewer # 1:

This manuscript reported the energy storage performance of MLCC with ultrahigh energy density and efficiency. For the real application of energy storage capacitor, real total amount of stored energy and applied voltage are more important than the energy density and electric field. In this regard, MLCC with thick film is very useful for real applications. If authors provide the total energy(J) and real applied voltage and emphasize the advantage of MLCC, then these information will be very useful for commercialization.

Response: We sincerely appreciate the reviewer's recognition of our work and the thoughtful comments emphasizing its relevance to practical energy storage applications. As you correctly pointed out, compared to single-layer ceramic capacitors, **MLCCs, with their multi-layer stacking architecture, can effectively meet the demand for higher capacitance in real-world electronic devices while maintaining a similar component count and volume.** In response to these valuable suggestions, we have highlighted this aspect in the revised manuscript to better emphasize the practical advantages of MLCCs for applications requiring higher energy storage.

It is precisely for this reason that our study focuses on the integration and miniaturization of MLCCs, aiming to enhancing energy storage performance while maintaining the same volume. Therefore, we have primarily used the total energy that can be stored per unit volume, i.e., energy density (J cm^{-3}), as the central metric of our study. This also represents a critical issue in the current field of dielectric energy storage research ^[1-4]. For commercial applications, the total energy (J) that the MLCCs can store benefits from precision equipment and other factors. As a result, MLCCs with thinner dielectric layers and more layers can store higher total energy (J), **especially when the energy density (J cm^{-3}) is high.** Furthermore, since the individual layer thickness of the MLCCs in this work is $\sim 7.5 \mu\text{m}$, applying a high voltage of 600 V across 5 layers in parallel enables efficient energy storage at this voltage level.

The references are as follows:

[1] Wang, G. et al. Electroceramics for high-energy density capacitors: current status and future perspectives. *Chem. Rev.* **121**, 6124 (2021).

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

[3] Li, D. et al. Progress and perspectives in dielectric energy storage ceramics. *J. Adv. Ceram.* **10**, 675-703 (2021).

[4] Yang, L. T. et al. Perovskite lead-free dielectrics for energy storage applications. *Prog. Mater. Sci.* **102**, 72-108 (2019).

1. BKNT + SST to modify the chemical composition. What is the reason to select the SST for example, similar atomic size and ferro/antiferro phase? It is strongly recommended to state the reason in more detail.

Response: We sincerely appreciate the reviewer's insightful question regarding the rationale for selecting Sr(Sc_{0.5}Ta_{0.5}O₃) (SST) as the compositional modifier. The introduction of SST into the BNKT matrix was deliberately designed to achieve multiple synergistic effects that are crucial for enhancing energy storage performance.

Firstly, the selection of Sr²⁺ (1.44 Å) as the A-site cation introduces further local disorder due to its size mismatch with Bi³⁺ (1.35 Å) and Na⁺ (1.39 Å), thereby amplifying the random electric field and aiding in the destabilization of macroscopic ferroelectric domains ^[1, 2]. In addition, Sr doping is well known to lower the Curie temperature, effectively broadening the operational temperature window of the material and enabling more thermally robust polarization behavior, which is desirable for wide-temperature-range applications ^[3, 4].

Meanwhile, based on charge neutrality and valence compensation considerations, a combination of Sc³⁺ and Ta⁵⁺ was selected to substitute for Ti⁴⁺ at the B-site. This aliovalent substitution introduces pronounced chemical and electrostatic disorder, further enhancing the random field effect and suppressing the formation of macroscopic ferroelectric domains. Moreover, the larger ionic radii of Sc³⁺ (0.75 Å) and Ta⁵⁺ (0.64

Å) compared to Ti^{4+} (0.61 Å), induce localized lattice expansion, offering greater freedom for ionic displacement under an applied electric field ^[1, 5].

From a macroscopic perspective, these structural modifications collectively contribute to the emergence of slim *P-E* loops with a largely improved maximum polarization (P_m) and negligible remnant polarization (P_r), enabling simultaneous enhancement in both recoverable energy density (W_{rec}) and energy efficiency (η). Furthermore, the wide bandgap associated with Ta_2O_5 (~ 4 eV) contributes to an elevated intrinsic breakdown strength (E_b), which is essential for sustaining high electric fields without premature dielectric failure ^[6].

In summary, to quantitatively assess the degree of compositional disorder introduced by multi-cation substitution, we adopted the concept of configurational entropy at the atomic level. This theoretical framework and its relevance to structural disorder and energy storage behavior are elaborated in the *Results and Discussion* section of the manuscript (Page 7). In response to the reviewer's constructive suggestion, we have further clarified and expanded this part in the revised version (see Supplementary Note 2).

The references are as follows:

[1] Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. A* **32**, 751-767 (1976).

[2] Zhao, W. C. et al. Broad-high operating temperature range and enhanced energy storage performances in lead-free ferroelectrics. *Nat. Commun.* **14**, 5725 (2023).

[3] Li, Y. et al. Enhanced energy storage performance in NBT-based MLCCs via cooperative optimization of polarization and grain alignment. *Nat. Commun.* **15**, 8958 (2024).

[4] Li, J. L. et al. Multilayer lead-free ceramic capacitors with ultrahigh energy density and efficiency. *Adv. Mater.* **30**, 1802155 (2018).

[5] Sun, Z. et al. Strong local polarization fluctuations enabled high electrostatic Energy Storage in Pb-Free Relaxors. *J. Am. Chem. Soc.* **146**, 13467-13476 (2024).

[6] Ma, L. et al. High energy storage density and efficiency in AgNbO₃ based relaxor antiferroelectrics with reduced silver content. *J. Eur. Ceram. Soc.* **43**, 3228-3235 (2023).

2. As the amount of SST increases, BKNT turned from FE to AFE to paraelectrics. Is it right? If authors provide the supporting data for this transition, that will be useful for other researchers to develop the higher energy density capacitors.

Response: It is indeed a topic of ongoing debate, particularly in BNT-based systems, whether a true AFE phase exists or if the observed features merely reflect relaxor-like or intermediate states ^[1, 2].

In our study, we observed that increasing the SST content in the BNKT system led to a progressive suppression of long-range ferroelectric ordering and the emergence of characteristics typically associated with relaxor or pseudo-antiferroelectric behavior, such as slim loops, reduced remnant polarization (P_r), and enhanced field-induced polarization. However, due to the lack of unambiguous double hysteresis loops or field-induced phase transitions that are characteristic of classical antiferroelectrics, we have refrained from explicitly labeling this intermediate state as “AFE”.

Instead, we interpret the observed evolution as a transition from ferroelectric (FE) to relaxor ferroelectric (REE) behavior, associated with the disruption of long-range polarization coherence. accompanied by a disruption of long-range ferroelectric domains. Supporting evidence for this transition, including, phase-field simulation results (Fig. 1, 2, original Supplementary Fig. 2, 3), temperature and frequency-dependent dielectric permittivity (Fig. 3a, original Supplementary Fig. 4a), and P - E loop analysis (Fig. 4b, original Supplementary Fig. 4b), has been systematically presented in Supplementary Information and discussed in *Results and Discussion* section (Page 8) of the manuscript.

We hope this clarification adequately addresses the reviewer's concern and provides useful context for interpreting the structural and functional transitions observed in our system.

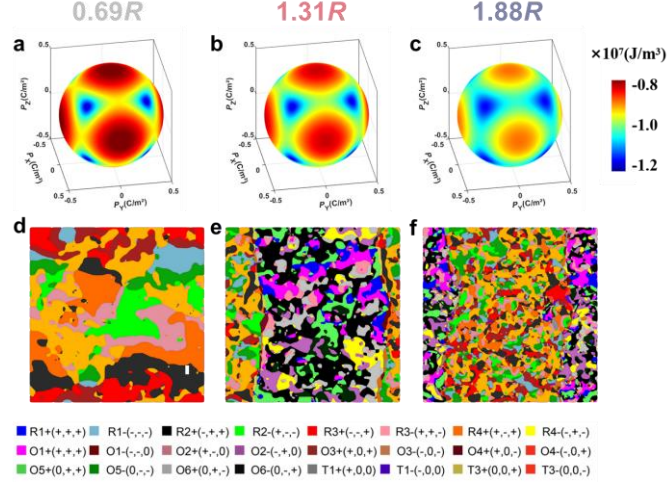


Fig. 1 Evolution of polar structures simulated by the phase-field model. (a to c) Landau free-energy profiles; (d to f) simulated domain structures for (a, d) 0.69R, (b, e) 1.31R, and (c, f) 1.88R. Among the phases, the R phase represents the lowest-energy state, while the T phase corresponds to the highest. Increasing doping levels reduce the Landau energy barrier, resulting in finer and more fragmented domain structures. Phase-field simulations account for the impact of doping-induced random fields, where the random orientation and normal distribution of field magnitudes give rise to domains of varying orientations, forming a mixed-phase configuration of R , O , and T domains (original Supplementary Fig. 2).

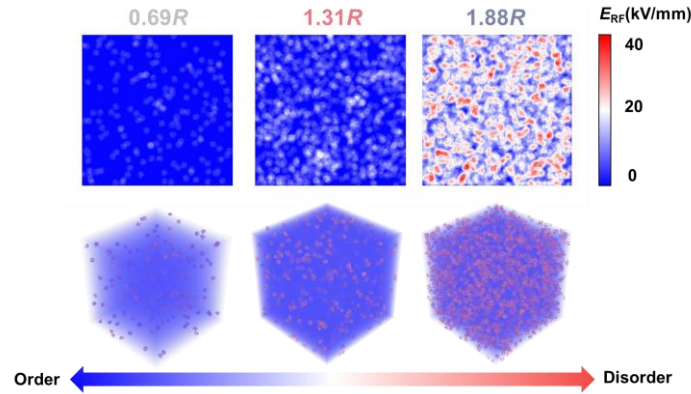


Fig. 2 The distribution of simulated random field in the X-Y plane and three-dimensional space for 0.69R, 1.31R, and 1.88R. With increasing configurational

entropy of the system, the intensity of the random field strengthens, and the degree of disorder intensifies (original Supplementary Fig. 3).

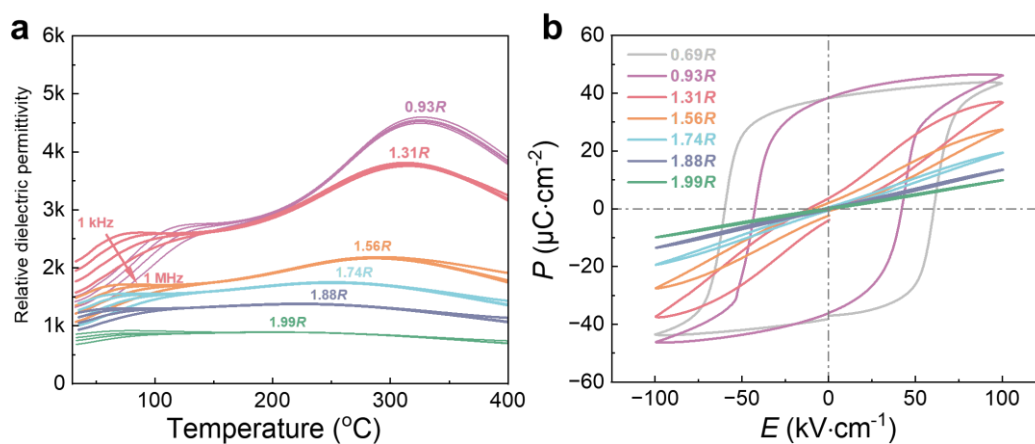


Fig. 3 Dielectric and ferroelectric properties of the BNT-based ceramics. a, Temperature and frequency-dependent dielectric spectra. b, Unipolar P-E hysteresis loops at 100 kV cm⁻¹ (original Supplementary Fig. 4).

The references are as follows:

[1] Zhou, X. et al. Phase structure and properties of sodium bismuth titanate lead-free piezoelectric ceramics. *Progress in Materials Science* **122**, 100836 (2021).

[2] Li, J. L. et al. Multilayer lead-free ceramic capacitors with ultrahigh energy density and efficiency. *Adv. Mater.* **30**, 1802155 (2018).

3. In the experimental, authors mentioned ‘pre-sintered powders’. What is the state of pre-sintered powders? Is it the calcined powder?

Response: We sincerely thank the reviewer for raising this clarification. The term “pre-sintered powders” used in the manuscript indeed refers to the calcined powders obtained after the solid-state reaction process. Specifically, the raw materials were thoroughly mixed and subjected to a calcination treatment at 850 °C for 4 hours in air to ensure complete phase formation and chemical homogeneity. To avoid confusion, we have revised the manuscript to replace “pre-sintered powders” with “calcined powders” in the relevant section of the experimental Methods.

4. Did you mix the polymer and ceramic powder altogether using high energy mill for 3 hours?

Response: We thank the reviewer for the pertinent question. Indeed, in our process, the calcined ceramic powders were mixed together with the organic constituents, including polymeric binders, plasticizers, and dispersants, using a high-energy ball mill operated at 1500 rpm for 3 hours. This procedure was deliberately implemented to ensure thorough homogenization, promote uniform dispersion of ceramic particles within the polymer matrix, and effectively eliminate entrapped air bubbles. Furthermore, the viscosity of the resulting slurry was carefully adjusted to ensure smooth casting and optimal green film quality. No evidence of polymer degradation or phase incompatibility was observed under the specified processing conditions.

5. The resultant MLCC green bodies were calcined at 360 °C for 8 hours: calcined? Following deblending, what does deblending mean?

Response: We appreciate the reviewer's attention to the clarity of terminology. We acknowledge that the term "calcined" at may have caused some confusion. In this context, "calcined" refers specifically to a low-temperature burnout process rather than a traditional high-temperature calcination used for phase formation. The purpose of this step is to thermally decompose and remove organic additives from the MLCC green bodies in a controlled manner, thereby minimizing the risk of cracking or delamination. Therefore, we have replaced "calcined" by "heated" in the revised manuscript to ensure greater clarity.

The phrase "following deblending" was used to indicate the post-burnout stage, i.e., after the organic additives have been removed. To avoid confusion, we have revised the wording in the manuscript to "following binder burnout", which more accurately reflects the process.

We thank the reviewer again for this helpful suggestion, and the revised manuscript has been updated accordingly to ensure clarity and precision.

6. For one hour: for 1 hour. Per min? min⁻¹: please unify the description of dimension. Authors should revise the MLCC fabrication process using the common nomenclature.

Response: We sincerely thank the reviewer for pointing out the inconsistency in the time and rate notations in the MLCC fabrication description. In response, we have carefully revised the relevant sections of the manuscript to ensure consistency and clarity in dimensional units throughout. Specifically: Time durations such as "for one hour" have been standardized to "for 1h"; Heating and pressing rates have been uniformly expressed using the standard notation " $^{\circ}\text{C min}^{-1}$ ", where applicable. All nomenclature related to the MLCC fabrication process has been revised according to widely accepted conventions in ceramic processing literature.

These revisions are reflected in the updated manuscript and highlighted accordingly. We appreciate the reviewer's attention to detail, which has helped improve the precision and readability of the manuscript.

7. Is this following procedure, right? ☐Tape casting ☐ Green body ☐ Warm isostatic pressing ☐ burn-out the organic ☐ CIP ☐ HIP ☐ silver pasting on both sides of the MLCC.

Response: We thank the reviewer for the careful reading and for summarizing the fabrication process. The described procedure is largely consistent with our fabrication process, but we would like to provide a few clarifications:

After the green ceramic tapes were prepared by tape casting, **Pt paste was screen-printed onto the tape surfaces to form internal electrodes prior to stacking**, which is a critical step in MLCC fabrication. The electrode-printed layers were then **precisely aligned and alternately stacked**, followed by **uniaxial pressing** (75 $^{\circ}\text{C}$, 30 MPa, 1h) and **warm isostatic pressing** (75 $^{\circ}\text{C}$, 120 MPa, 40 min) to ensure good interfacial contact between layers.

Next, the **organic burnout** process was carried out at 360 $^{\circ}\text{C}$ for 8 hours with a controlled heating rate of 0.5 $^{\circ}\text{C min}^{-1}$ to thoroughly remove organic constituents. The resulting green bodies were then subjected to **cold isostatic pressing (CIP) at 200 MPa for 15 minutes** to further eliminate residual porosity and enhance green density. Final sintering was performed at 1030-1150 $^{\circ}\text{C}$ for 2 h, followed by **hot isostatic pressing**

(HIP) at 1000 °C for 1 h to further improve densification. **After polishing the sides to expose the internal electrodes**, silver paste was applied to both ends to form outer electrodes for electrical measurements.

8. This process is not common for MLCC. Why did not you make the Pt electrodes in the beginning? How did you connect each electrode in the layer?

Response: In fact, this process represents a commonly employed protocol for MLCC fabrication at the laboratory scale, with only minor variations in specific operational details. The full procedure is schematically illustrated in Fig. 4 for clarity.

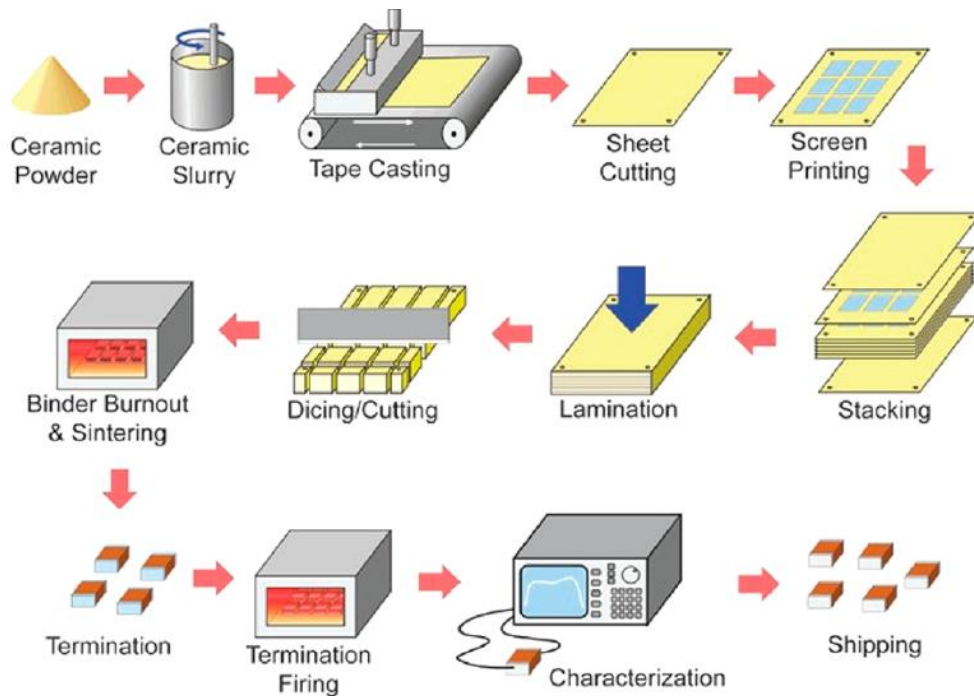


Fig.4 The schematic diagram of the MLCCs fabrication process ^[1].

Regarding the reviewer's question about why the Pt electrodes were not made at the beginning, we would like to clarify that the Pt internal electrodes were indeed screen-printed onto each green ceramic tape prior to the stacking step. This approach is fully consistent with both laboratory- and industry-scale MLCC fabrication ^[2]. This step is essential for integrating internal electrodes layer-by-layer, allowing for precise control over the electrode geometry and alignment during the lamination process.

If the reviewer's question pertains to why the Pt electrodes were not co-processed with the ceramic slurry during the initial tape-casting step, the main reason lies in geometric and processing limitations. Specifically, co-casting Pt paste with the dielectric slurry often results in poor thickness control and irregular electrode geometry, which compromises the precision required for layer alignment during stacking. Such issues are particularly detrimental to the miniaturization and integration of devices. Therefore, applying Pt electrodes via screen printing after tape casting is a more viable approach, as it ensures better control over electrode thickness and pattern uniformity, thereby maintaining the structural integrity and performance reliability of the final MLCCs.

To ensure effective interconnection among the multilayer electrodes, the sintered MLCCs were polished on both lateral surfaces to expose the ends of the internal Pt electrodes, followed by silver paste application. This step electrically connects all electrode layers in parallel and establishes the external terminals for electrical testing.

The references are as follows:

[1] Wang, G. et al. Electroceramics for high-energy density capacitors: current status and future perspectives. *Chem. Rev.* **121**, 6124 (2021).

[2] Li, J. L. et al. Grain-orientation-engineered multilayer ceramic capacitors for energy storage applications. *Nat. Mater.* **19**, 999-1005 (2020).

9. Are the fig (data) from MLCC sample or bulk sample? The process for bulk sample and MLCC is different each other, then the microstructure is also different resulting to the different properties.

Response: As correctly pointed out by the reviewer, the processing routes for bulk ceramics and MLCCs differ significantly, which can lead to distinct differences in microstructure and, consequently, functional properties. This distinction is, in fact, one of the key conclusions and motivations of our study. In this work, bulk ceramic and repeated rolling processed (RRP) samples with identical compositions were used primarily as comparative benchmarks to evaluate the improvements and optimizations

resulting from the prototypical multilayer device fabrication. The corresponding data and microstructural analyses for these samples have been separately defined and labeled in both the main text and the Supplementary Information. For example, “1.88R-BC” refers to the bulk ceramic sample, “1.88R-RRP” denotes the sample fabricated via repeated rolling processing, and “1.88R-MLCCs” corresponds to the final multilayer capacitor device. Detailed figure captions are also provided to ensure an unambiguous distinction among the different sample types.

10. In the fig. 1, authors draw the polar region with small arrow. Is this a domain? Then what is the grain? IF there were no grain, then sample should not show XRD pattern like glass.

Response: We apologize for any confusion caused.

Firstly, we would like to clarify that the three schematic illustrations in Fig. 1a represent distinct structural scales, progressing from long-range ferroelectric (FE) order to polar nanoregions (PNRs), and finally to unit-cell-scale polar units characteristic of the polar glass state (PGS). Specifically, the gray blocks in the left panel denote individual grains, with the blue long arrows illustrating macroscopic FE domains. The middle panel, showing oval-shaped features of varying orientations, represents spatially confined and dynamically disordered PNRs with different activity levels. The right panel displays unit-cell-scale polar entities (green ellipses), signifying the local polarization sections induced by the PGS strategy. As stated in the manuscript, “the PGS strategy aims to break local FE ordering and transform PNRs into atomic-range polarization sections, enhancing total polar displacement at the unit cell range to disturb long-range polar order, albeit some strongly localized polarizations may vanish.”

Secondly, we emphasize that this figure is a conceptual framework and does not imply the absence of grains. On the contrary, well-defined grains are clearly observed in SEM micrographs (see Fig. 5, original Supplementary Fig. 21), confirming the presence of a polycrystalline structure.

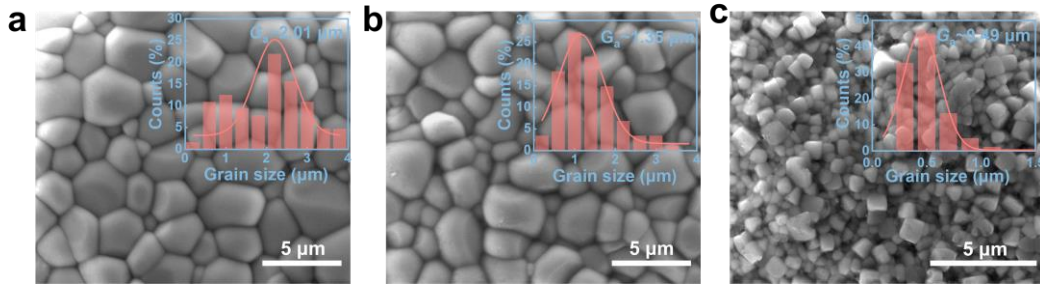


Fig. 5 Natural surfaces SEM morphology and grain size distribution. a, 1.88R-BC, b, 1.88R-RRP, and c, 1.88R-MLCCs (original Supplementary Fig. 21).

Thirdly, it is important to clarify that the polar glass state (PGS) reflects a nanoscale or atomic-scale short-range disordered polarization configuration. It does not correspond to a structurally amorphous or glassy phase in the conventional crystallographic sense. Rather, it is analogous to the concept of a "dipole glass" widely used in the field of relaxor ferroelectrics^[1, 2]. In contrast, XRD captures long-range average crystallographic order. Indeed, as the reviewer correctly points out, the retention of well-defined diffraction peaks in the XRD patterns confirms the preservation of long-range crystallographic order at the lattice level. This is entirely consistent with the concept of relaxor ferroelectrics, in which local structural or polar disorder is superimposed on an overall crystalline matrix. Therefore, the presence of a polar glass state does not contradict the observation of clear XRD reflections. Instead, it reinforces the coexistence of local disorder and long-range order, a hallmark of many relaxor ferroelectric systems previously reported in the literature^[3, 4].

The references are as follows:

[1] Fu, J. et al. A highly polarizable concentrated dipole glass for ultrahigh energy storage. *Nat. Commun.* **15**, 7338 (2024).

[2] Li, F. et al. Local structural heterogeneity and electromechanical responses of ferroelectrics: learning from relaxor ferroelectrics. *Adv. Funct. Mater.* **28** 1801504 (2018).

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

[4] Yang, L. T. et al. Perovskite lead-free dielectrics for energy storage applications. *Prog. Mater. Sci.* **102**, 72-108 (2019).

11. To support the small polar region (small arrow in Fig. 1c), authors should indicate the region in the TEM image.

Response: Thank you for your valuable suggestion. In fact, as is shown in Fig. 6, we have conducted HR-TEM analysis on the BNT (0.69R), 1.88R-BC, and 1.88R-MLCCs samples. The results reveal that in BNT ceramics, ordered stripe domains with widths of 200 nm and 300 nm are observed within the grains, indicating strong ferroelectricity. In the 1.88R-BC sample, polar nanoregions (PNRs) were observed, confirming the enhancement of relaxor behaviors. However, in the 1.88R-MLCCs sample, no local contrast or visual evidence of chemical aggregation associated with polar nanoregions was found, indicating the absence of aggregated nanoscale chemical or polar clusters. Due to the resolution limitations of conventional HR-TEM, this region could not be indicated in the image, which is why we did not include these HR-TEM images for discussion in the manuscript. However, this observation indirectly supports our argument that the polar glass state (PGS) promotes atomic-scale chemical heterogeneity and "freezes" the local disordered state, preventing the material from further equilibrating and transforming into nanoscale polar microregions. We will include this analysis in the revised manuscript and highlight the relevant findings.

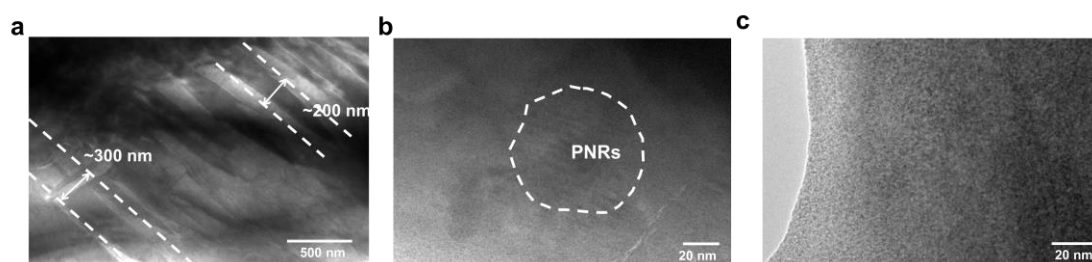


Fig. 6 HR-TEM micrographs of a BNT, b, 1.88R-BC, and c, 1.88R-MLCCs

To further explore the fine structural features, especially in terms of polar structures and local characteristics, we employed aberration-corrected STEM which provides higher resolution. **Extensive in situ STEM characterizations were**

conducted to better understand this local polar heterogeneity, and these results are thoroughly discussed in both the original main text and Supporting Information.

Thank you again for your insightful feedback.

Responses to Reviewer # 2:

The authors implemented a polar glass state (PGS) strategy to enhance the energy storage performance of BNT-based multilayer ceramic capacitors (MLCCs) by modulating dynamic and thermodynamic processes. This approach reduced hysteresis loss, improved breakdown strength, and optimized nano-domain disruption and grain refinement through hierarchical structural engineering. As a result, the capacitors achieved an ultra-high recoverable energy density (W_{rec}) of 22.92 J/cm³ and an exceptional efficiency (η) of 97.1%, along with superior high-temperature stability. The proposed strategy provides a transformative blueprint for developing next-generation dielectric capacitors for high-temperature applications. Below are some comments which should be addressed properly before resubmission.

Response: We greatly appreciate the reviewer for her/his time to review our manuscript and give us the above encouraging comments. The enlightening suggestions are very helpful for improving the clarity, rigor, and overall quality of the research presented. Thus, we have revised our manuscript accordingly.

1. Does the proposed polar glass state (PGS) strategy sufficiently explain the enhancement observed in energy storage performance? Are there alternative mechanisms that could contribute to the improved breakdown strength and reduced hysteresis loss? Need further discussion. Refine introduction portion. Few other refs may be useful in refining introduction and cite them at appropriate places:

<https://doi.org/10.1016/j.jallcom.2017.10.126>

<https://doi.org/10.1088/1361-6463/aa7fa7>

<https://doi.org/10.1016/j.jmat.2021.12.007>

<https://doi.org/10.1016/j.matlet.2021.130577>

<https://doi.org/10.1063/1.5021410>

<https://doi.org/10.1088/1361-6463/aaada1>

Response: We sincerely appreciate the reviewer's thoughtful feedback and constructive suggestions. First and foremost, we would like to clarify that clarify that

the Polar Glass State (PGS) strategy provides a localized explanation for the structural stability and energy storage performance of the MLCCs prototype devices we have developed. Indeed, on the order of approximately 5 nm, polar nanoregions still retain certain ferroelectric (FE) characteristics, which can lead to residual fields ^[1]. This accounts for the observed increase in polarization hysteresis and the corresponding decrease in efficiency (η) at relatively high electric fields. The PGS strategy aims to destabilize local FE ordering and transform PNRs into atomic-scale polarization units, thereby enhancing the total polar displacement within the unit cell and further disrupting long-range polarization order in the PNRs structure. In an ideal PGS, each unit cell exhibits a degree of spontaneous polarization, and the polarization distribution is spatially non-uniform, resulting in a more averaged polarization magnitude across the material. This strategy also promotes atomic-scale chemical heterogeneity and “freezes” the disordered state locally, thereby preventing further equilibration and transition into nanoscale polar microregions. Under high electric fields, the PGS strategy not only preserves a larger maximum polarization ($P_{\max}$) but also effectively suppresses P_r , which is essential for achieving high recoverable energy density (W_{rec}) and a field-insensitive efficiency (η).

In addition to the localized mechanism provided by the PGS strategy, we have conducted comprehensive studies, including in situ XRD and X-ray total scattering (XPDF analysis), to investigate the temperature stability of both long-range and short-range structures in the 1.88R-MLCCs. Furthermore, phase-field simulations at the mesoscopic scale were performed to explore the evolution of the material's polar structure with temperature, validating the thermal stability of domain structures. Additionally, we employed SEM at the grain scale and piezoelectric force microscopy at the micro/nano scale to elucidate the mechanisms behind the improved breakdown strength and reduced hysteresis loss, which are thoroughly discussed in the manuscript.

In light of the reviewer's suggestion, we have refined the introduction to emphasize the role of the PGS strategy in optimizing both the local and global structural features that contribute to improved energy storage performance. Furthermore, we have incorporated the references suggested by the reviewer to better support the discussion

of these mechanisms, ensuring a thorough and well-rounded explanation of the factors driving the enhanced performance in our materials ^[2-5]. We believe that these revisions address the reviewer's comments and provide a clearer understanding of the underlying factors contributing to the improved performance of our MLCCs.

The references are as follows:

[1] Fu, J. et al. A highly polarizable concentrated dipole glass for ultrahigh energy storage. *Nat. Commun.* **15**, 7338 (2024).

[2] Banerjee, K. & Asthana, S. Scaling behavior of different shapes of hysteresis loops and recoverable energy storage density in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, and $\text{Na}_{0.25}\text{K}_{0.25}\text{Bi}_{0.5}\text{TiO}_3$ ferroelectrics. *J. Materiomics* **8**, 918-927 (2022).

[3] Niranjana, M. K. et al. Randomly arranged cation-ordered nanoregions in lead-free relaxor ferroelectric $\text{K}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$: Prediction from first-principles study. *J. Appl. Phys.* **123** 244106 (2018).

[4] Karthik, T. et al. Nature of electric field driven ferroelectric phase transition in lead-free $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$: In-situ temperature dependent ferroelectric hysteresis and Raman scattering studies. *J. Alloys Compd.* **732**, 945-951 (2018).

[5] Banerjee, K. & Asthana, S. Role of polar nanoregions in the enhancement of the recoverable energy storage density and electrostrictive coefficient in the lead free $\text{Na}_{0.25}\text{K}_{0.25}\text{Bi}_{0.5}\text{TiO}_3$. *Mater. Lett.* **304** 130577 (2021).

2. There are many works in MLCCs which have prominent results as compared to the present data. The author needs to explore more and comparative discussion should be provided.

Response: We sincerely thank the reviewer for this comment. Firstly, while we acknowledge that several high-performance MLCCs have indeed been reported in recent years, we would like to respectfully point out that the majority of these studies focus on lead-based systems ^[1]. Given the environmental and regulatory concerns associated with lead-containing materials, our work is specifically centered on the development of high-performance lead-free MLCCs. Accordingly, lead-based MLCCs fall outside the primary scope of our comparative analysis.

Secondly, we would like to emphasize that, as explicitly stated in both the title and the core discussion of our manuscript, the central objective of our work is to achieve a synergistic enhancement of recoverable energy density (W_{rec}) and energy efficiency (η) for MLCCs over a broad operating temperature range (25 °C to 150 °C). Most existing studies, particularly those reporting very high W_{rec} values, tend to focus solely on room-temperature performance and often exhibit substantial degradation in efficiency at high temperatures. For instance, Wang et al. achieved an ultra-high W_{rec} ($> 25 \text{ J}\cdot\text{cm}^{-3}$) in a NaNbO_3 -based system; however, the energy efficiency remained below ($< 80\%$) and dropped to $\sim 60\%$ at 150 °C [2]. While such results are commendable in terms of a single performance metric, they lack the integrated high-temperature reliability essential for practical applications. Therefore, such cases were not prioritized in our main comparative discussion.

Based on the above principles, our original manuscript already provides an extensive comparative analysis of the high-temperature energy storage characteristics of MLCCs, with a particular focus on integrated performance metrics (see Fig.1, original Supplementary Fig. 9). Nevertheless, in response to the reviewer’s constructive suggestion, we have carefully reviewed and analyzed additional recent literature and, based on the aforementioned selection criteria, incorporated several newly published studies into the revised manuscript to further strengthen the comparative context. Notably, as is shown in Fig. 2 and Fig. 3, while some of these reports show excellent room-temperature energy storage performance, their high-temperature stability remains inferior to that demonstrated in our work [3, 4].

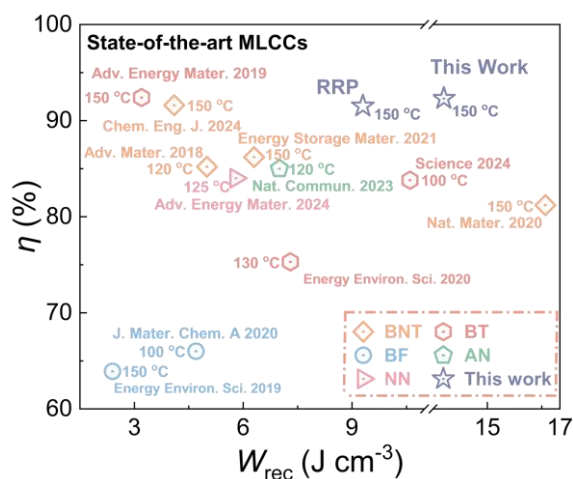


Fig. 1 Comparisons of W_{rec} versus η (100 ~ 150 °C) between our work (including 1.88R-RRP) with the most recently reported lead-free MLCCs (original Supplementary Fig. 9).

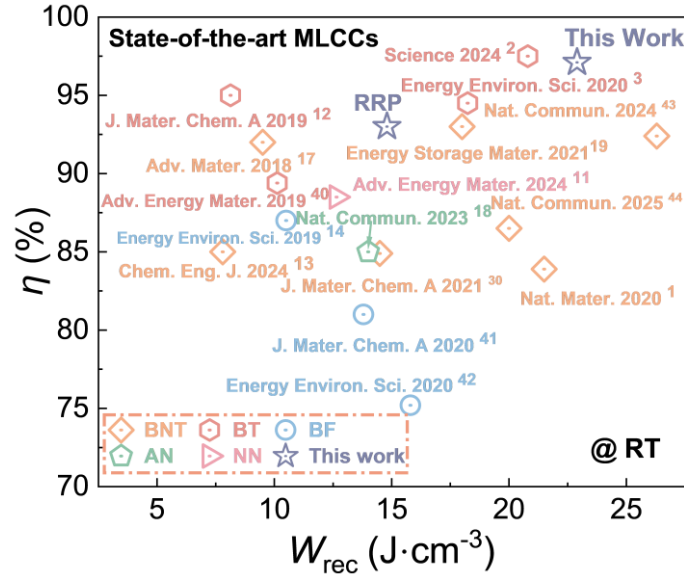


Fig.2 Comparisons of W_{rec} and η between our work (including 1.88R-RRP) with the state-of-the-art lead-free MLCCs at room temperature.

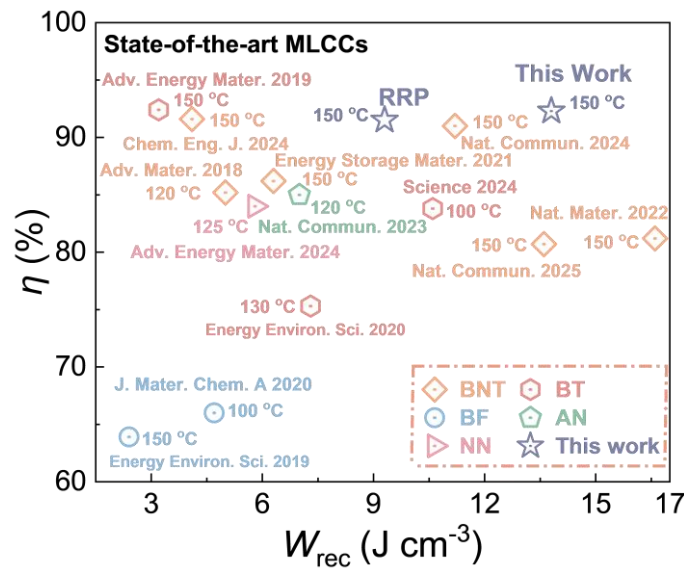


Fig.3 Comparisons of W_{rec} versus η (100 ~ 150 °C) between our work (including 1.88R-RRP) with the most recently reported lead-free MLCCs.

The references are as follows:

[1] Li, D. et al. Progress and perspectives in dielectric energy storage ceramics. *J. Adv. Ceram.* **10**, 675-703 (2021).

[2] Wang, X. et al. Lead-free high permittivity quasi-linear dielectrics for giant energy storage multilayer ceramic capacitors with broad temperature stability. *Adv. Energy Mater.* **14**, 2400821 (2024).

[3] Fu, J. et al. A highly polarizable concentrated dipole glass for ultrahigh energy storage. *Nat. Commun.* **15**, 7338 (2024).

[4] Li D. et al. Global-optimized energy storage performance in multilayer ferroelectric ceramic capacitors. *Nat. Commun.* **16**, 188 (2025).

3. Free energy curve is not needed to discuss elaborately. I felt disconnected.

Response: We sincerely appreciate the reviewer's thoughtful feedback. While we understand the concern regarding the discussion of the free energy curve, we respectfully believe it provides important physical insight that directly supports the central mechanisms proposed in this study. The inclusion of the free energy schematic is not intended as an abstract thermodynamic exposition, but rather serves as a concise conceptual framework to illustrate how entropy-induced polarization disorder, in particular the quasi-stationary disorder associated with the formation of the polar glass state (PGS), modifies the evolution of the energy barrier and thereby contributes to the observed enhancement in energy storage performance.

In particular, the adoption of schematic free energy or Landau-type potentials to represent local energy barrier variations is well-established in the literature for describing field-induced phase transitions and domain switching behaviors in relaxor ferroelectrics and dielectric energy storage materials ^[1-4]. This approach provides a clear and intuitive thermodynamic perspective for understanding polarization mechanisms, one can better understand the polarization disorder and its connection to macroscopic energy storage properties. In our case, this visualization helps bridge theoretical understanding with the experimental observations of low remanent polarization (P_r), high recoverable energy density (W_{rec}), and near-linear polarization responses under high electric fields.

In response to the reviewer's concern, we have revised the corresponding section of the manuscript to enhance clarity and conciseness, and to better align it with the

experimental findings and the underlying design rationale. We hope this revision more clearly conveys the scientific relevance of the free energy schematic in the context of the PGS-enhanced energy storage mechanism.

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).

[2] Pan, H. et al. Ultrahigh-energy density lead-free dielectric films via polymorphic nanodomain design. *Science* **365**, 578-582 (2019).

[3] Oses, C., Toher, C. & Curtarolo, S. High-entropy ceramics. *Nat. Rev. Mater.* **5**, 295-309 (2020).

[4] Hsu, W. L. et al. Clarifying the four core effects of high-entropy materials. *Nat. Rev. Chem.* **8**, 471-485 (2024).

4. Why 1.88R-MLCCs have porosity and provide thermal itching surface morphology?

Response: We appreciate the reviewer's observation and apologize for any confusion it may have caused. We would like to clarify that the darker contrast regions observed in the SEM micrographs of the 1.88R-MLCCs are not indicative of pores, but instead results from topographical variations at the grain level. Differences in grain height and inclination angles lead to localized differences in secondary electron yield under low-acceleration SEM imaging, which visually appear as darker regions ^[1]. This effect is commonly observed during SEM characterization of as-sintered ceramic surfaces, where topographical variations at the grain level give rise to contrast differences unrelated to actual porosity. ^[2]. In fact, as demonstrated in Fig. 4 (original Supplementary Fig. 21), the 1.88R-MLCC exhibits a finer grain size and significantly improved microstructural densification compared to both the 1.88R-bulk ceramic (BC) and the counterpart fabricated via repeated rolling processing (RRP). This refined microstructure is precisely why the 1.88R-MLCCs demonstrate superior breakdown strength (E_b) and energy storage performance (see Fig. 5, original Fig. 2c).

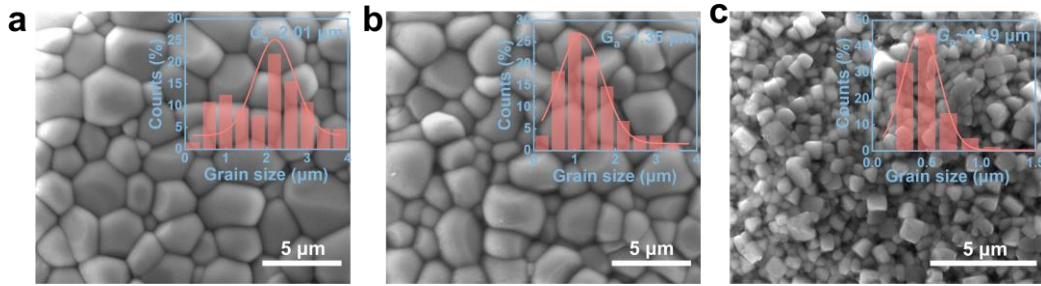


Fig. 4 Natural surfaces SEM morphology and grain size distribution. a, 1.88R-BC, b, 1.88R-RRP, and c, 1.88R-MLCCs (original Supplementary Fig. 21).

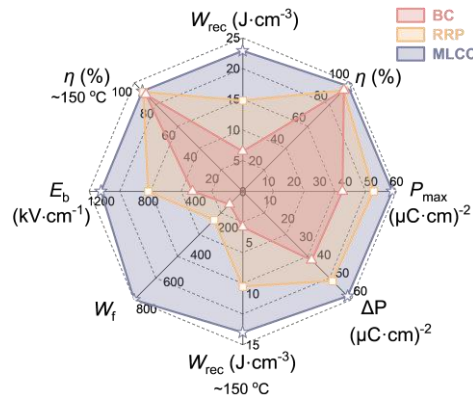


Fig. 5 Comparisons of comprehensive properties for 1.88R-MLCCs, 1.88R-BC, and 1.88R-RRP (original Fig. 2c).

In response to the reviewer's concern, we have conducted additional thermal etching characterization of the 1.88R-MLCCs surface, as shown in the newly provided figure (Fig. 6). The corresponding image has been included in the revised Supplementary Information file, and relevant discussion has been incorporated into the highlighted sections.

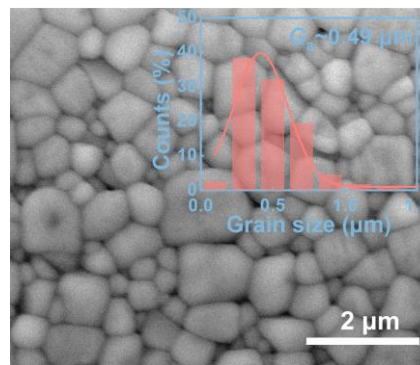


Fig. 6 Thermal etching surface morphology and grain size distribution of 1.88R-MLCCs

The references are as follows:

[1] Dyck, O. et al. Contrast mechanisms in secondary electron e-beam-induced current imaging. *Microsc. Microanal.* **28**, 1567-1583 (2022).

[2] Yang, J., Zhao, Y., Zhu, L. & Hao, X. Enhanced electrocaloric effect of relaxor potassium sodium niobate lead-free ceramic via multilayer structure. *Scripta Mater.* **193**, 97-102.

5. Describe the relationship between the structural variation and the difference in polarization values between them.

Response: We sincerely thank the reviewer for this insightful question. The polarization differences observed among the 1.88R-BC, 1.88R-RRP, and 1.88R-MLCC samples can be directly attributed to the structural variations induced by their respective processing routes. Although the composition remains constant, the distinct fabrication methods lead to different thermodynamic and kinetic conditions during sintering and densification, resulting in varied microstructural features. In general, finer grain structures result in a higher density of grain boundaries. These grain boundaries serve as pinning centers that hinder ferroelectric domain wall motion and disrupt long-range ferroelectric order. Under an applied electric field, dipoles in a fine-grained structure must reorient primarily by rotating within their local domains (since domain wall movement is impeded), which requires less energy per dipole reorientation^[1]. However, this mechanism contributes less to the overall polarization, effectively lowering the dielectric constant of the material^[2, 3]. As a result, the maximum polarization (P_m) shows a decreasing trend from 1.88R-BC to 1.88R-RRP to 1.88R-MLCC under the same applied electric field.

The references are as follows:

[1] Zhao, W. C. et al. Broad-high operating temperature range and enhanced energy storage performances in lead-free ferroelectrics. *Nat. Commun.* **14**, 5725 (2023).

[2] Li, D. et al. A high-temperature performing and near-zero energy loss lead-free ceramic capacitor. *Energy & Environmental Science* (2023).

[3] Li, Y. et al. Enhanced energy storage performance in NBT-based MLCCs via cooperative optimization of polarization and grain alignment. *Nat. Commun.* **15**, 8958 (2024).

6. How does the hierarchical structural engineering approach specifically influence the nano-domain disruption and grain refinement? Try high-resolution microscopy or in-situ techniques provide further insights into these structural modifications.

Response: Thank you for your valuable suggestion. In fact, as is shown in Fig. 7, we have conducted HR-TEM analysis on the BNT (0.69R), 1.88R-BC, and 1.88R-MLCCs samples. The results reveal that in BNT ceramics, ordered stripe domains with widths of 200 nm and 300 nm are observed within the grains, indicating strong ferroelectricity. In the 1.88R-BC sample, polar nanoregions (PNRs) were observed, confirming the enhancement of relaxor behaviors. However, in the 1.88R-MLCCs sample, no local contrast or visual evidence of chemical aggregation associated with polar nanoregions was found, indicating the absence of aggregated nanoscale chemical or polar clusters. Due to the resolution limitations of conventional HR-TEM, this region could not be indicated in the image, which is why we did not include these HR-TEM images for discussion in the manuscript. However, this observation indirectly supports our argument that the polar glass state (PGS) promotes atomic-scale chemical heterogeneity and "freezes" the local disordered state, preventing the material from further equilibrating and transforming into nanoscale polar microregions. We will include this analysis in the revised manuscript and highlight the relevant findings (see Supplementary Fig. 2).

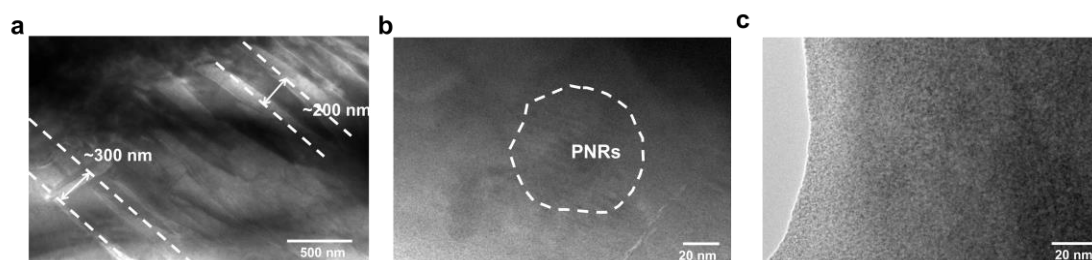


Fig. 7 HR-TEM micrographs of a BNT, b, 1.88R-BC, and c, 1.88R-MLCCs

To further explore the fine structural features, especially in terms of polar structures and local characteristics, we employed aberration-corrected STEM which provides higher resolution. **Extensive in situ STEM characterizations were conducted to better understand this local polar heterogeneity, and these results are thoroughly discussed in both the original main text and Supporting Information (please refer to original Fig. 3, original Supplementary Fig. 17, 18).**

In addition to the localized mechanism provided by the PGS strategy, we have conducted comprehensive studies, including in situ XRD (see **original Fig. 4c, Supplementary Fig. 20**) and X-ray total scattering combined with XPDF analysis (see **original Fig. 4b**), to investigate the temperature stability of both long-range and short-range structures in the 1.88R-MLCCs. Furthermore, phase-field simulations at the mesoscopic scale were performed to explore the evolution of the material's polar structure with temperature, validating the thermal stability of domain structures (see **original Fig. 4e**). Additionally, we employed SEM (**original Supplementary Fig. 21**) at the grain scale and piezoelectric force microscopy (**original Supplementary Fig. 4d**) at the micro/nano scale to elucidate the mechanisms behind the improved breakdown strength and reduced hysteresis loss, which are thoroughly discussed in the manuscript.

7. The study claims state-of-the-art high-temperature stability. What are the precise operational temperature limits of the MLCCs, and how do they compare them with commercially available dielectric capacitors in terms of energy density and efficiency at elevated temperatures?

Response: We apologize for any confusion caused. When we refer to state-of-the-art high-temperature stability, we specifically mean a **comprehensive evaluation of energy storage performance at high temperatures** in comparison to other recently reported lead-free MLCCs that are renowned for their excellent thermal stability ^[1-11].

Firstly, as shown in Fig. 8a (please refer to Fig. 2e in the original manuscript), within the temperature range from 25 °C to 150 °C, the recoverable energy density ($W_{\text{rec}} \approx 14.21 \pm 0.63 \text{ J} \cdot \text{cm}^{-3}$) of our 1.88R-MLCCs remains remarkably stable, with minimal fluctuation in efficiency ($\Delta\eta/\eta \leq 2\%$). This result outperforms a range of lead-free

recently reported MLCCs known for their superior temperature stability (Fig. 8b, original Fig. 2f) [1-7].

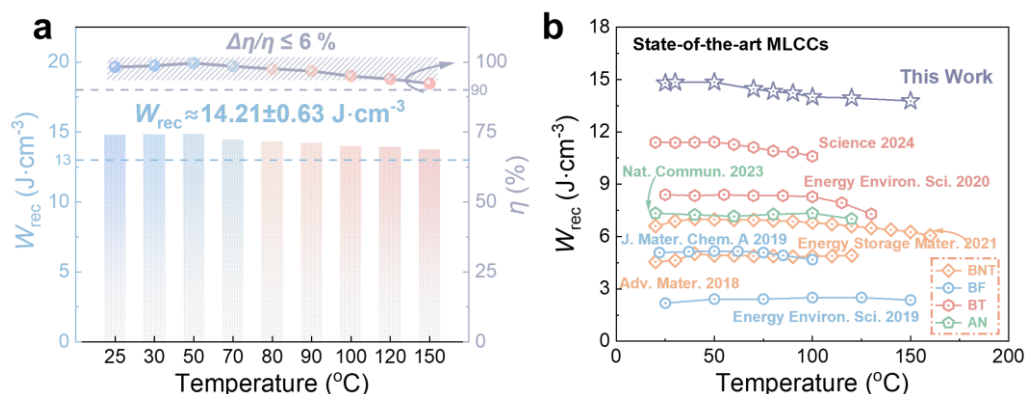


Fig. 8 Thermal stability of 1.88R-MLCCs. a Temperature-dependent energy storage performance at an electric field of 800 kV cm^{-1} (original Fig. 2e). b Comparison of recoverable energy density across a wide operating temperature range between our study and other reported advanced MLCCs (original Fig. 2f).

Secondly, the 1.88R-MLCCs exhibit robust high-field endurance, sustaining electric fields up to 800 kV cm^{-1} at 150°C . This exceptional field tolerance enables the 1.88R-MLCCs to maintain outstanding energy storage performance under high-temperature conditions, with a recoverable energy density (W_{rec}) of $\sim 13.77 \text{ J cm}^{-3}$ and an energy efficiency (η) of $\sim 92.3\%$ ($>90\%$) at 150°C (Fig. 9, original Supplementary Fig. 9) [1-11]. These metrics outperform the high-temperature energy storage characteristics of recently reported high-end lead-free MLCC systems.

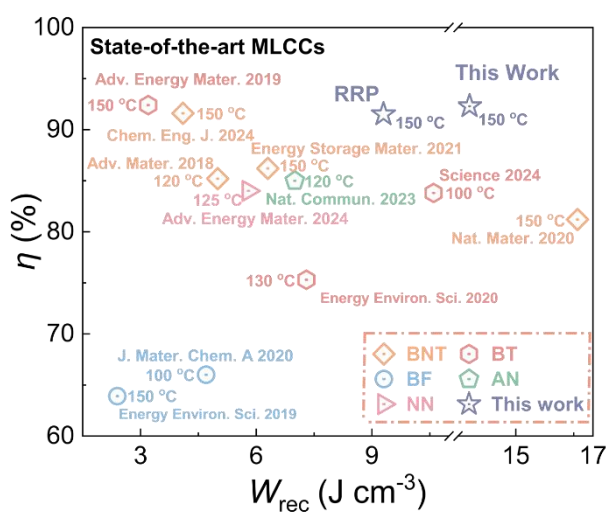


Fig. 9 Comparisons of W_{rec} versus η (100 ~ 150 °C) between our work (including 1.88R-RRP) with the most recently reported lead-free MLCCs.

Thirdly, we evaluated the high-temperature cyclic overdamped discharge behavior of the 1.88R-MLCCs under an electric field of 800 kV·cm⁻¹ at 120 °C. (Fig. 10, original Supplementary Fig. 13, and Fig. 2h). The results reveal excellent cycling stability over 10⁵ charge-discharge cycles, with negligible performance degradation. It is worth noting that most previous studies have primarily focused on discharge characteristics at room temperature, whereas our work extends this evaluation to elevated temperatures.

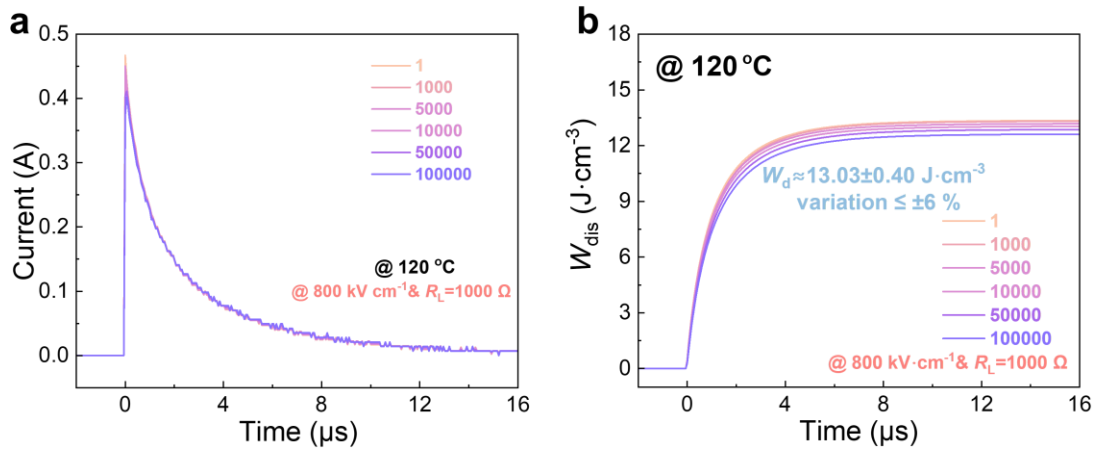


Fig. 10 The high-temperature cyclic overdamped discharge properties of 1.88R-MLCCs. Cycling stability (1-10⁵) of (a) overdamped discharging current (original Supplementary Fig. 13) and (b) discharge energy density as a function of time under 800 kV cm⁻¹ at 120 °C (original Fig. 2h).

In summary, **our study demonstrates a leading position in terms of comprehensive energy storage performance under high-temperature conditions, with advantages in thermal stability, field endurance, and cycling reliability.**

As for the precise operational temperature limit of the MLCCs, we believe that **the concept of a limit temperature is inherently generalized and should be defined in conjunction with specific performance criteria.** Nevertheless, to provide a more concrete assessment, we performed additional *P-E* loops measurements under an applied electric field of 800 kV cm⁻¹. When the temperature reaches 200 °C (see Fig. 11), the 1.88R-MLCC still exhibits measurable energy storage capability ($W_{\text{rec}} \approx 13.43$ J·cm⁻³), the energy efficiency drops below 90% (~88.6%). Therefore, **we consider 200 °C**

to be the practical upper temperature limit for maintaining high-efficiency performance ($\geq 90\%$).

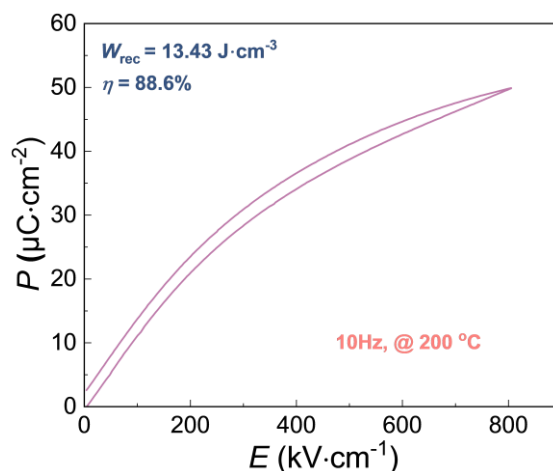


Fig. 11 Unipolar P - E loop of **1.88R-MLCCs under 800 kV cm^{-1}** at $200 \text{ }^{\circ}\text{C}$.

Indeed, for commercially available Class II (BaTiO_3 -based) ceramic capacitors industrial standards predominantly emphasize the thermal stability of capacitance (or dielectric constant), rather than evaluating metrics such as recoverable energy density and energy efficiency, which are rarely evaluated or reported, especially under high-temperature conditions. Specifically, the X7R standard defines an upper operating temperature limit of $125 \text{ }^{\circ}\text{C}$, with a requirement that the capacitance variation remains within $\pm 15\%$ relative to its room-temperature value (i.e., $\Delta C/C_{25 \text{ }^{\circ}\text{C}} \leq \pm 15\%$). The X8R and X9R classifications raise this upper temperature requirement for capacitance stability to $150 \text{ }^{\circ}\text{C}$ and $200 \text{ }^{\circ}\text{C}$, respectively. To facilitate a meaningful comparison, we conducted additional analysis on the temperature-dependent dielectric behavior of the 1.88R-MLCCs, which show a stable capacitance ($\Delta C/C_{25 \text{ }^{\circ}\text{C}} \leq \pm 15\%$) up to approximately $170 \text{ }^{\circ}\text{C}$ (Fig. 12). We appreciate your commitment to ensuring the scientific rigor and relevance of the study and will incorporate this new result in the revised version of the manuscript.

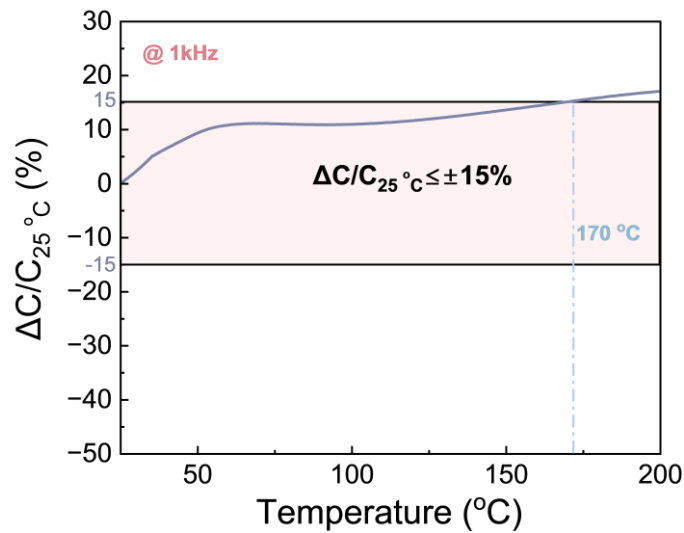


Fig.12 Variation of temperature-dependent capacitance deviation ($\Delta C/C_{25\text{ }^{\circ}\text{C}}$) at 1 kHz.

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).

[2] Zhao, P. Y. et al. Ultra-high energy storage performance in lead-free multilayer ceramic capacitors via a multiscale optimization strategy. *Energy Environ. Sci.* **13**, 4882-4890 (2020).

[3] Wang, G. et al. Ultrahigh energy storage density lead-free multilayers by controlled electrical homogeneity. *Energy Environ. Sci.* **12**, 582-588 (2019).

[4] Li, J. L. et al. Multilayer lead-free ceramic capacitors with ultrahigh energy density and efficiency. *Adv. Mater.* **30**, 1802155 (2018).

[5] Zhu, L. F. et al. Heterovalent-doping-enabled atom-displacement fluctuation leads to ultrahigh energy-storage density in AgNbO₃-based multilayer capacitors. *Nat. Commun.* **14**, 1166 (2023).

[6] Ji, H. F. et al. Ultrahigh energy density in short-range tilted NBT-based lead-free multilayer ceramic capacitors by nanodomain percolation. *Energy Storage Mater.* **38**, 113-120 (2021).

[7] Wang, G. et al. Fatigue resistant lead-free multilayer ceramic capacitors with ultrahigh energy density. *J. Mater. Chem. A* **8**, 11414-11423 (2020).

[8] Li, J. L. et al. Grain-orientation-engineered multilayer ceramic capacitors for energy storage applications. *Nat. Mater.* **19**, 999-1005 (2020).

[9] Lv, Z. Q. et al. NaNbO₃-based multilayer ceramic capacitors with ultrahigh energy storage performance. *Adv. Energy Mater.* **14**, 2304291 (2024).

[10] Li, Y. et al. Improving the electric energy storage performance of multilayer ceramic capacitors by refining grains through a two-step sintering process. *Chem. Eng. J.* **479**, 147844 (2024).

[11] Zhao, P. Y. et al. High-performance relaxor ferroelectric materials for energy storage applications. *Adv. Energy Mater.* **9**, 1803048 (2019).

8. How feasible is the large-scale fabrication of BNT-based MLCCs with the PGS strategy? What are the key processing challenges, and how do they impact the reproducibility and manufacturing cost of these capacitors?

Response: We thank the reviewer for raising this important practical consideration. Regarding the feasibility of large-scale fabrication of BNT-based MLCCs employing the PGS strategy, it is indeed promising due to the compatibility of this approach with existing industrial MLCCs production processes. The synthesis and processing steps involved, such as conventional solid-state reaction and tape-casting procedures (see Fig. 13), are well-established and broadly utilized in the commercial MLCC industry, underscoring the scalability potential of the proposed approach.

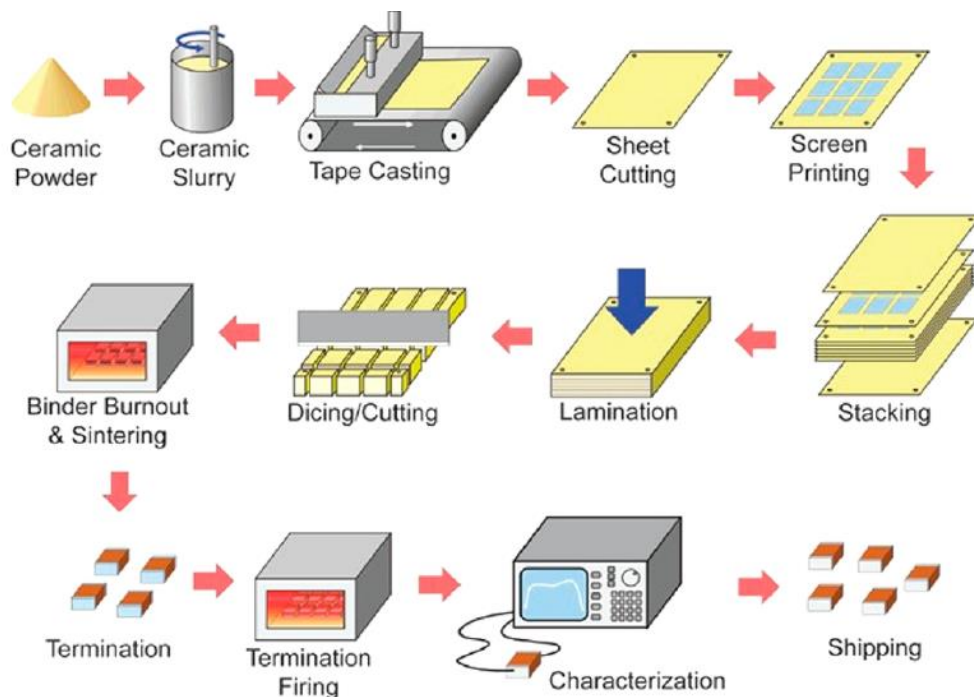


Fig. 13 The schematic diagram of the MLCCs fabrication process. ^[1]

Nevertheless, certain processing challenges must be carefully managed to ensure reproducibility and cost-effectiveness at industrial scales. These challenges primarily include:

(1) achieving **consistent chemical homogeneity** during large-batch ceramic powder preparation;

(2) maintaining precise control of **sintering atmospheres and profiles** to avoid compositional volatility or defect formation, and ensuring rigorous control over **microstructural uniformity** (e.g., grain size distribution and densification); and

(3) optimizing the **tape-casting slurry formulation**, especially with regard to viscosity control, to enable defect-free tape formation and uniform layer thickness during large-scale processing.

All of these factors play a critical role in determining the stability of dielectric properties and the reliability of final MLCC devices, thus directly affecting product reproducibility and manufacturing yield ^[2].

Regarding manufacturing costs, since the proposed **PGS strategy leverages standard ceramic processing techniques without requiring specialized or excessively high-cost equipment, the incremental cost compared to conventional BNT-based ceramic fabrication should remain modest**. Furthermore, careful optimization of processing parameters and rigorous quality control measures are essential to mitigate variability, thereby enhancing reproducibility and ultimately maintaining a competitive manufacturing cost.

In summary, while technical challenges remain, as is typical for any lab-to-industry transition, they are surmountable through targeted process optimization. Overall, the PGS strategy presents a scalable and economically viable pathway for the development of high-performance, lead-free MLCCs.

The references are as follows:

[1] Wang, G.et al. Electroceramics for high-energy density capacitors: current status and future perspectives. *Chem. Rev.* **121**, 6124 (2021).

[2] Li D. et al. Global-optimized energy storage performance in multilayer ferroelectric ceramic capacitors. *Nat. Commun.* **16**, 188 (2025).

9. While the work demonstrates excellent performance metrics, have accelerated lifetime tests (such as fatigue, thermal cycling, or humidity resistance) been conducted to assess the long-term reliability of these MLCCs under real-world operating conditions?

Response: We sincerely appreciate the reviewer's insightful comment regarding the long-term reliability of the fabricated MLCCs. As you mentioned, we have conducted comprehensive accelerated lifetime evaluations, including **fatigue endurance and thermal cycling assessments, which were described in detail in the original submission.**

Specifically, as shown in Fig. 14 (please refer to Supplementary Fig. 10 and Fig. 2d in the original manuscript), **fatigue reliability assessment** was carried out on the 1.88R-MLCCs under an applied electric field of 800 kV cm^{-1} at ambient temperature. The results reveal exceptional cycling durability, with energy storage performance (both W_{rec} and η) exhibiting negligible degradation ($<1\%$) throughout the cycling tests over 10^5 cycles.

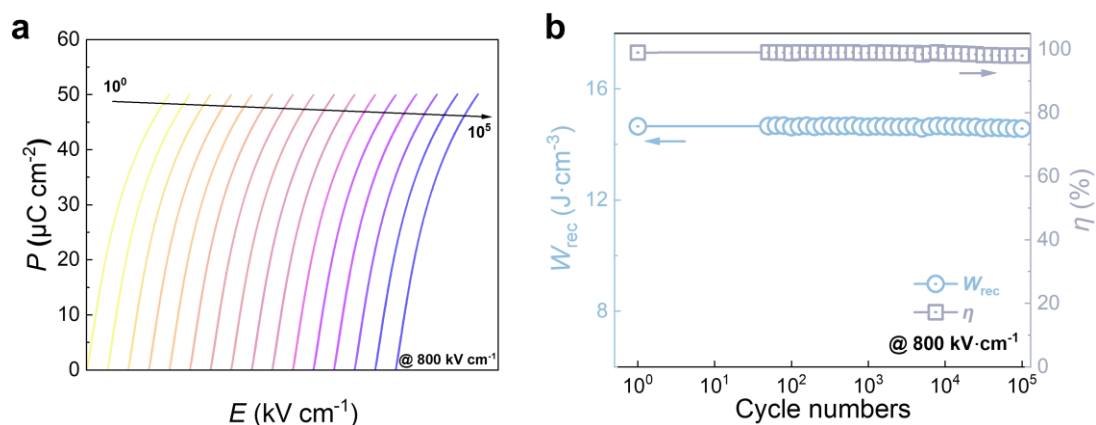


Fig. 14 Fatigue reliability assessment of 1.88R-MLCCs. a Unipolar P-E hysteresis loops of as a function of the cycling numbers ($1-10^5$) (Original Supplementary Fig. 10) and b cycle numbers-dependent energy storage performance under 800 kV cm^{-1} (original Fig. 2d).

Furthermore, we performed **temperature-dependent P - E loops measurements** on the 1.88R-MLCCs at 800 kV cm^{-1} for a **thermal stability assessment**, revealing that both the P_{max} values (Fig.15a, original Supplementary Fig. 11) and energy storage performance (Fig.15b, original Fig. 2e) remained virtually stable across a broad temperature range ($25 \sim 150 \text{ }^{\circ}\text{C}$). Of particular significance is that 1.88R-MLCCs not only exhibit temperature insensitivity but also achieve an unprecedentedly high W_{rec} ($\approx 14.21 \pm 0.63 \text{ J}\cdot\text{cm}^{-3}$) with minimal efficiency fluctuation ($\Delta\eta/\eta \leq 2\%$), surpassing an array of cutting-edge lead-free MLCCs known for their superior temperature stability (original Fig. 2f). These achievements underscore the considerable potential of 1.88R-MLCCs for advanced energy storage applications in demanding environmental conditions.

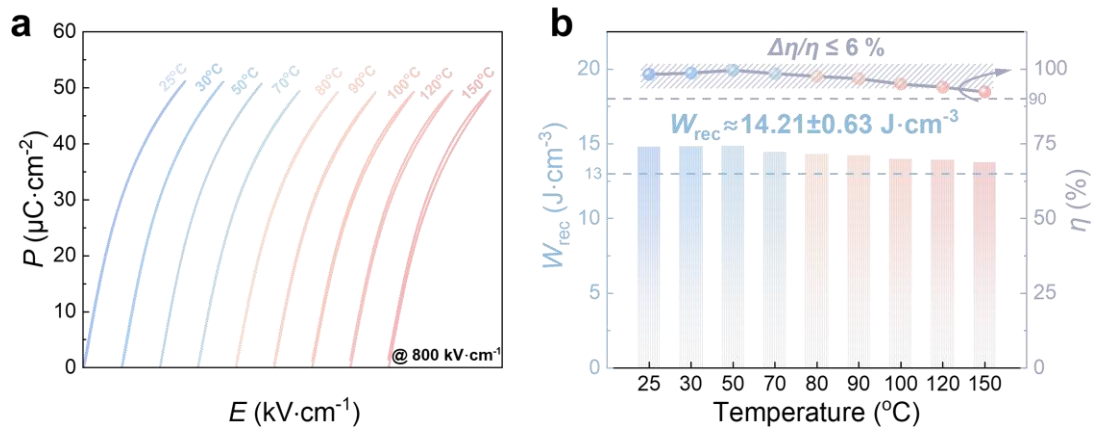


Fig. 15 Thermal stability assessment of 1.88R-MLCCs. a Temperature-dependent unipolar P - E hysteresis loops (original Supplementary Fig. 11) and b energy storage performance at an electric field of 800 kV cm^{-1} (original Fig. 2e).

In addition to the W_{rec} and η , a key criterion for evaluating the viability of high-power pulsed electronic components is their charge/discharge performance. We further investigated **the high-temperature (@120 $^{\circ}\text{C}$) cyclic overdamped discharge properties** (Fig.16, original Supplementary Fig. 13 and Fig. 2h) at 800 kV cm^{-1} . The results demonstrate exceptional cycling stability during the charge-discharge processes (10^5 cycles), with minimal variation in W_{d} ($\sim 13.03 \pm 0.40 \text{ J}\cdot\text{cm}^{-3}$), further highlighting their robustness under elevated temperature conditions.

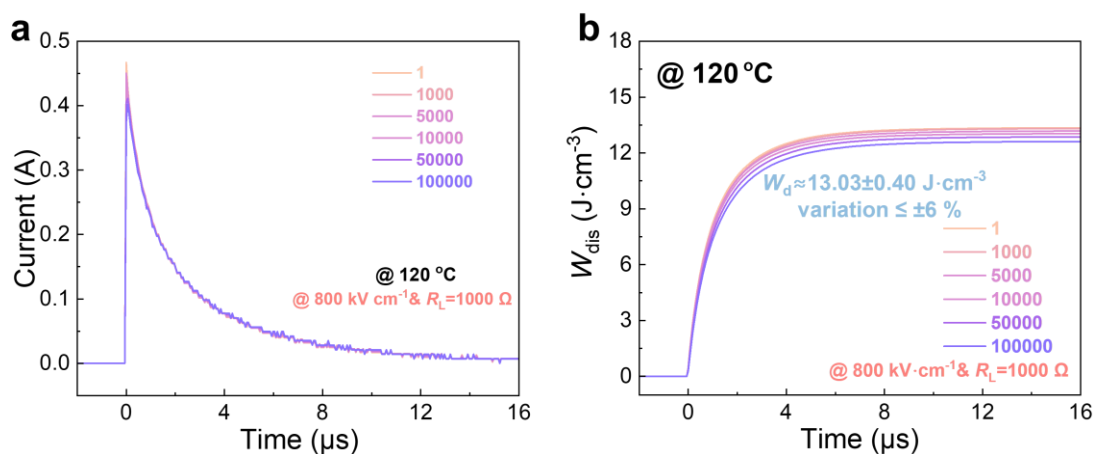


Fig. 16 The high-temperature cyclic overdamped discharge properties of 1.88R-MLCCs. Cycling stability ($1\text{-}10^5$) of (a) overdamped discharging current (original Supplementary Fig. 13) and (b) discharge energy density as a function of time under 800 kV cm^{-1} at $120 \text{ }^\circ\text{C}$ (original Fig. 2h).

As correctly pointed out by the reviewer, we fully concur that humidity resistance testing is also critical for comprehensively evaluating MLCC reliability. However, humidity resistance assessments were not included within the scope of the current study, as **our primary research objective focused explicitly on intrinsic electrical fatigue endurance and thermal reliability**. Moreover, humidity resistance evaluations have frequently been overlooked within the current dielectric energy-storage research community; even top-tier studies published in renowned journals such as *Science*, *Nature*, and *Nature Materials* generally lack this form of assessment ^[1-5]. **This indicates a broader absence of standardized humidity-testing protocols within the field, further underscoring the significance and timeliness of the reviewer’s suggestion.**

In summary, we fully recognize the importance of humidity stability, and firmly believe the reviewer’s valuable suggestion will significantly promote more comprehensive and standardized reliability assessments in the future. **Such enhanced assessments will benefit not only MLCCs but also the broader dielectric energy-storage community.** Nevertheless, **we would like emphasize that the primary objectives of our current study were the enhancement of intrinsic electrical fatigue endurance and thermal stability, through which we achieved unprecedented**

breakthroughs in energy-storage performance, particularly an ultrahigh recoverable energy density coupled with exceptional temperature stability. In future research, we intend to explore feasible approaches to systematically address humidity-related reliability issues, aiming to provide a more robust foundation for practical application and long-term stability of dielectric materials and devices.

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).

[2] Pan, H. et al. Ultrahigh-energy density lead-free dielectric films via polymorphic nanodomain design. *Science* **365**, 578-582 (2019).

[3] Chen, J. et al. Ladderphane copolymers for high-temperature capacitive energy storage. *Nature* **615**, 62-66 (2023).

[4] Yang, B. B. et al. High-entropy enhanced capacitive energy storage. *Nat. Mater.* **21**, 1074-1080 (2022).

[5] Li, J. L. et al. Grain-orientation-engineered multilayer ceramic capacitors for energy storage applications. *Nat. Mater.* **19**, 999-1005 (2020).

10. Cite some of the recent publications in energy storage paper. (<https://doi.org/10.1016/j.jallcom.2022.167340>, <https://doi.org/10.1016/j.est.2024.112020>, <https://doi.org/10.1016/j.mseb.2023.117038>, <https://doi.org/10.1016/j.jallcom.2024.17827>).

Response: Thank you for your valuable suggestion. In the revised manuscript, we have incorporated four recent and representative publications relevant to dielectric energy storage, as suggested. These works provide important insights into the latest advances in relaxor ferroelectrics, multilayer ceramic capacitors, and help contextualize our research within the current state-of-the-art. **The references have been added in the Introduction and Discussion sections.**

Responses to Reviewer # 3:

The manuscript studies the energy storage properties of sodium bismuth titanate (NBT)-based multilayer capacitors. Due to a poor description of the methodology, it is impossible to reproduce any of the formulations in either bulk or multilayer form, as well as some of the experiments. The insufficient quality of the data makes the conclusions of this paper unreliable.

Response: We express our gratitude to you for the time and effort in examining our manuscript. However, we respectfully and strongly disagree with the assertion that “due to a poor description of the methodology, it is impossible to reproduce any of the formulations in either bulk or multilayer form,” and that “the insufficient quality of the data makes the conclusions of this paper unreliable.” **Such a sweeping judgment overlooks the extensive methodological clarity and multi-scale validation presented throughout the manuscript and the Supplementary Information.**

Firstly, regarding methodological reproducibility:

All essential experimental details are clearly and reproducibly described in both the main manuscript and the Supporting Information. Specifically:

Sample formulations and compositions are explicitly provided, including detailed stoichiometry of all BNKT-xSST variants ($x = 0$ to 0.25).

Raw materials and processing conditions (including bulk ceramic and Repeated rolling processing) such as precursor identity, ball-milling parameters, calcination and sintering temperatures, times, atmospheres, and equipment are clearly listed.

Multilayer ceramic capacitors (MLCCs) fabrication protocols are thoroughly explained, including tape-casting conditions, screen-printing of internal Pt electrodes, stacking alignment procedures, lamination pressure, organic burnout settings, cold/hot isostatic pressing schedules, sintering regimes, and final Ag terminal electrode application.

Given this level of detail, we firmly believe our methodology is sufficiently described to enable reproduction by other experts in the field. **We also wish to note that, considering the brief review timeframe, it is highly unlikely the reviewer**

attempted experimental reproduction of the various ceramic forms described. Therefore, the claim that “it is impossible to reproduce any of the formulations” appears to be speculative rather than based on scientific evaluation or empirical verification.

Secondly, regarding data quality and the reliability of conclusions:

We also respectfully disagree with the assertion that the data presented in our study lack the quality to support the conclusions. On the contrary, **our findings are firmly in high-quality experimental data acquired through comprehensive structural and functional evaluations spanning atomic, mesoscopic, and macroscopic scales.** These include, but are not limited to:

Comprehensive experimental evidence: The energy storage performance is supported by *P-E* hysteresis loops, dielectric constant measurements across temperature and frequency ranges, Weibull statistical analysis of dielectric breakdown strength, as well as charge-discharge cycling, fatigue endurance tests, and thermal cycling evaluations.

Multi-scale structural validation: The relationship between structure and performance is systematically established via advanced characterization techniques. These include: In situ Aberration-corrected STEM, which confirm the evolution of domain structures; In situ synchrotron XRD and X-ray total scattering (XPDF), which reveal temperature-dependent long- and short-range structural stability; Phase-field simulations, which elucidate mesoscopic domain evolution mechanisms with thermal variation; SEM and PFM imaging, which capture structural features at both grain and nanoscale levels.

Correlation and benchmarking: The trends in polarization, breakdown strength, and energy density are explained through well-established structure–property relationships. Our findings are also benchmarked against state-of-the-art literature for lead-free MLCCs, demonstrating that both the magnitude and reproducibility of our energy storage metrics are competitive and credible.

Taken together, the structural insights, electrical measurements, and modeling outcomes are coherent and mutually reinforcing. As such, we firmly believe that the

quality of our data is sufficient to justify the conclusions drawn in the manuscript. Additionally, in response to the reviewer's suggestion, we have further optimized the presentation of several data sets in the revised version to improve clarity and eliminate any potential ambiguity.

We trust that these clarifications and enhancements address the reviewer's concerns, and we remain committed to the highest standards of transparency and scientific rigor.

1. The strategy to achieve the polar glass state, as explained on p. 6 is to control the chemical heterogeneity and to balance between thermodynamics and kinetics ('dynamics') upon sintering. While chemical heterogeneity is achieved by inserting four A-site and three B-site cations with different charges into the perovskite lattice, it is not explained how thermodynamics and kinetics are controlled or balanced upon sintering. It is written on the same page that the polar glass state is achieved by the sintering conditions (T and t). However, this is not later developed in the results section. Then, on p. 7, it is written that as opposed to polar nanoregions, atomic scale polarisation is achieved in the study. It is not evident how and why ferroelectric and antiferroelectric interactions arise. In brief, the strategy described at the beginning of the results section is not convincingly confirmed in later parts.

Response: We sincerely thank the reviewer for pointing out the need for greater clarity in explaining our strategy for achieving the polar glass state (PGS) and its confirmation in the results.

Clarification of the PGS Strategy : The PGS strategy is based on two key principles. First, we introduce chemical heterogeneity by incorporating four A-site and three B-site cations with varying valences into the perovskite lattice, which induces strong local compositional disorder and initiates the formation of polar nano-regions (PNRs). Second, and critically, we precisely control the sintering temperature and duration to balance the thermodynamic and kinetic processes. This control allows the system to remain in a non-equilibrium state, suppressing the development of long-range

polar order and stabilizing a PGS characterized by atomic-scale, randomly distributed polarizations.

Specifically, the sintering parameters are tuned to allow sufficient atomic diffusion to generate chemical heterogeneity, while limiting the thermodynamic equilibration that would otherwise lead to local ordering. This “freezing” of the system at an intermediate state prevents the formation of thermodynamically stable PNRs and yields a spatially disordered polarization structure. The detailed sintering conditions and their effects on structure and properties are presented in the Methods section and Supplementary Note 2.

Evidence Supporting the PGS Mechanism in the Results Section:

1. Structural and Microstructural Characterization

STEM Analysis: Atomic-resolution STEM images (Fig. 3a, Supplementary Figs. 17-21) reveal no discernible PNRs. Instead, the spontaneous atomic displacement vectors exhibit random orientations and similar magnitudes throughout the structure. This isotropic distribution directly supports the PGS model, indicating the suppression of long-range polar correlations.

Temperature-Dependent Observations: In-situ STEM (Fig. 3, Supplementary Fig. 21) and X-ray total scattering with PDF analysis (Fig. 4b) demonstrate that the atomic-scale disordered polarization remains stable up to 150 °C, confirming the thermal robustness of the PGS.

3. Local Field and Polarization Distribution

Phase-Field Simulations: Simulations (Supplementary Fig. 3, 4) show that chemically induced local fields disrupt long-range order, leading to disordered nanoscale domain structures and reduced energy barriers. This enhances configurational entropy and matches the characteristics of a PGS.

X-ray Total Scattering: In-situ PDF analysis (Fig. 4b) shows preserved local structural features with increasing temperature, without evidence of chemical clustering or phase separation. This confirms the spatial inhomogeneity and stability of the PGS.

Addressing Ferroelectric and Antiferroelectric Interactions

The PGS state arises from the frustration between local ferroelectric (FE) and antiferroelectric (AFE) interactions. Chemical heterogeneity and non-equilibrium sintering suppress the dominance of either interaction, resulting in a pseudo-conjugated local field landscape. Each unit cell retains some spontaneous polarization, but the overall structure remains statistically non-polar. This effect is confirmed by the random, isotropic atomic displacement vectors observed via STEM (Fig. 3) and the flattened Landau free energy landscape shown in phase-field simulations (Supplementary Fig. 3).

2. When discussing energy storage, the breakdown field plays a significant role. It is known from the literature that the dielectric breakdown field (or strength) is inversely proportional to several material parameters. It decreases with increasing element thickness, grain size, presence of secondary phases, porosity (fraction and pore size), electrode size, temperature and so on. It is thus not evident what the purpose of comparing the samples prepared by different routes is or, in other words, why show the radar graph in Figure 2c. Presumably, the samples had different thermal budgets, which are not specified well enough. It is worth noting that the sintering temperatures and times are given as temperature ranges, such as 1030 – 1150 °C for MLCCs. The samples had different microstructures, and they behaved differently in terms of their energy storage properties. It is worth noting that the microstructures should be prepared following conventional metallographic procedure, i.e., polishing and etching.

Response: Thank you for your thoughtful comments. We agree that the dielectric breakdown strength is strongly dependent on various microstructural and extrinsic factors such as thickness, grain size, porosity, and processing conditions. In this work, the comparison between 1.88R bulk ceramics (BC), repeated rolling processing (RRP), and MLCCs is not intended to directly correlate breakdown strength to a specific microstructural parameter. Rather, the purpose of this comparison is to demonstrate how our compositionally optimized system performs under different processing routes and structural hierarchies, highlighting its scalability and potential from fundamental material development to practical device-level applications.

The radar graph in Figure 2c is intended to provide a comprehensive and intuitive comparison of the overall energy storage performance of the different samples. It visually represents multiple key performance metrics, including W_{rec} , η , E_b , P_{max} , ΔP , and their performance at elevated temperatures ($W_{\text{rec}} \sim 150$ °C and $\eta \sim 150$ °C). This graphical representation allows for a quick and clear comparison of the trade-offs between different properties across the samples. The radar graph clearly shows that 1.88R-MLCCs exhibit significant improvements in all performance metrics, particularly at high temperatures, highlighting the effectiveness of the tape-casting and stacking method in optimizing energy storage properties.

As the reviewer rightly pointed out, differences in sintering conditions result in distinct microstructures and, consequently, variations in energy storage behavior. Our designed compositions exhibit good densification over a wide temperature range (1030-1150 °C). In line with your suggestion, we have now clearly stated the optimized sintering condition used for MLCCs. In line with your suggestion, we have now clearly specified the optimized sintering condition used for the MLCC samples, which is 1100 °C for 2 hours, in the revised manuscript.

Additionally, the microstructural characterization of MLCCs was conducted following standard metallographic practices. We performed polishing and thermal etching on the natural surfaces of the samples. The grain size distributions obtained from these treated surfaces were statistically analyzed using Nano Measurer software, and the results are consistent with those reported earlier based on surface morphology (see Fig.1, Supplementary Fig. 24).

We appreciate the reviewer's valuable feedback, which helped us further clarify the methodology and rationale behind our comparative analysis.

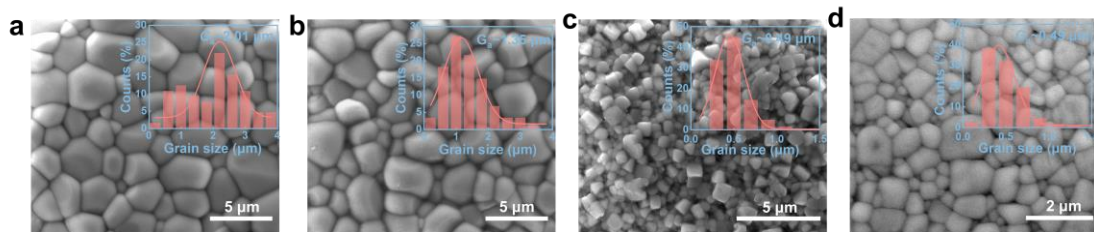


Fig. 1 SEM morphology and grain size distribution. Natural surfaces SEM morphology of a, 1.88R-BC, b, 1.88R-RRP, and c, 1.88R-MLCCs, along with d, thermal etching surface morphology of 1.88R-MLCCs (Supplementary Fig. 24).

3. It would be necessary to include the dielectric permittivity data (real and imaginary parts) in broader temperature and frequency ranges. Similarly, it would be helpful to measure the P - E loops also at lower temperatures. Figure S4 does not provide enough data for a reliable assessment of the nature of the studied materials.

Response: We thank the reviewer for this comment. In our original study, we measured the temperature and frequency-dependent dielectric permittivity (both real and imaginary parts) from room temperature to 400°C. The primary objective of Figure S4a was to intuitively illustrate the impact of different configurational entropies on the dielectric properties and relaxation behavior of the materials. In response to the reviewer's suggestion, we have now included the temperature-dependent dielectric permittivity and $\tan\delta$ data for all compositions at various frequencies in the revised supplementary information (see Fig. 2, Supplementary Fig. 5).

We would like to clarify that our study is primarily concerned with energy storage behavior at ambient to elevated temperatures. The dielectric spectra were collected to qualitatively assess the impact of configurational entropy on dielectric response and relaxor behavior over this targeted temperature range, and extending the frequency ranges further would not substantially impact the core conclusions of this work. Dielectric and ferroelectric measurements at sub-ambient temperatures fall outside the intended scope of this study and are not expected to significantly influence the interpretation or conclusions, which focus on high-temperature energy storage performance.

Nevertheless, we appreciate the reviewer's perspective and will consider a broader temperature range in future studies where low-temperature performance becomes a key concern.

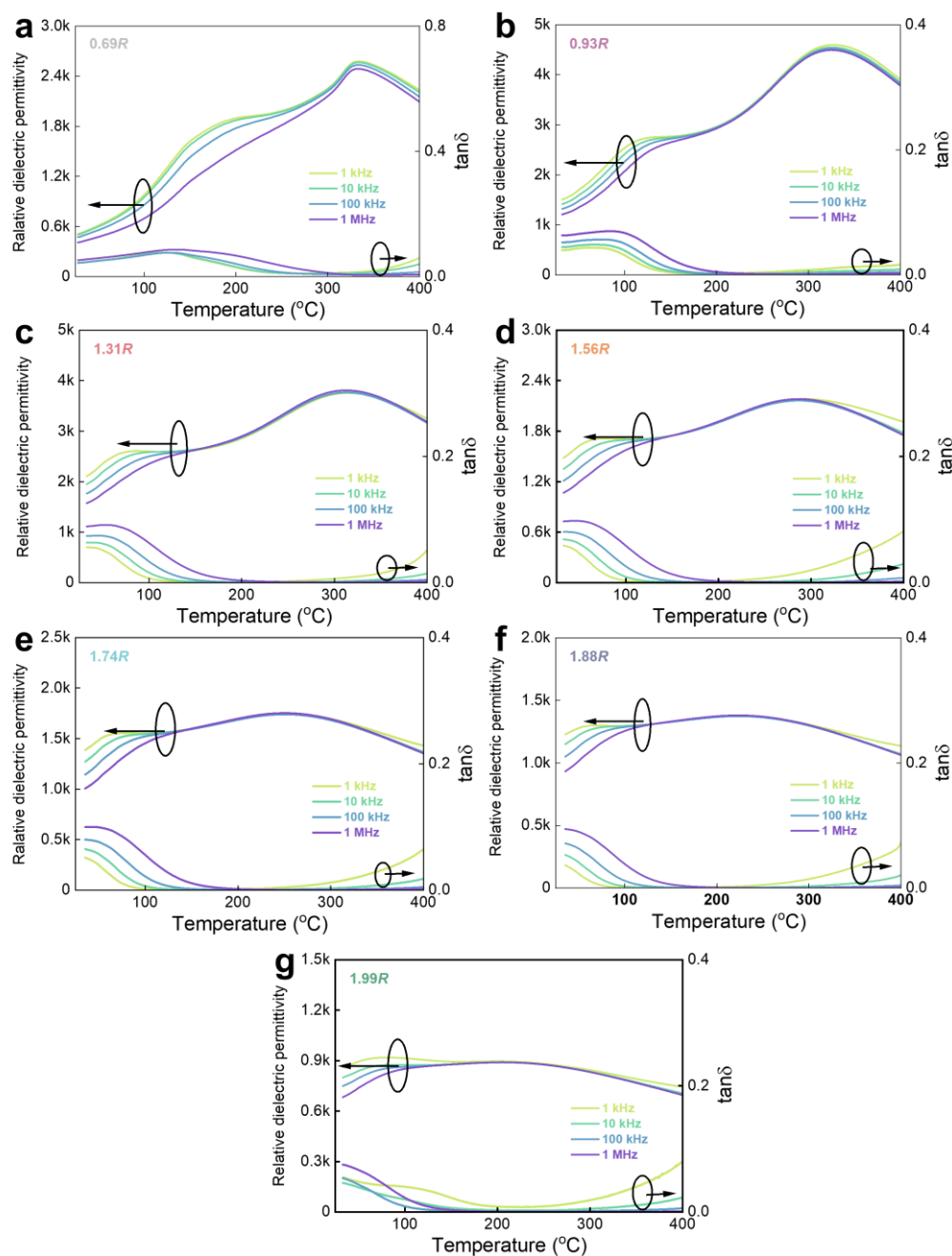


Fig.2 Temperature-dependent dielectric permittivity and $\tan\delta$ with different frequencies for the a BNT (0.69R) and (1-x)BNKT-xSST ceramics: b $x = 0$ (0.93R), c $x = 0.05$ (1.31R), d $x = 0.10$ (1.56R), e $x = 0.15$ (1.74R), f $x = 0.20$ (1.88R), g $x = 0.25$ (1.99R) (Supplementary Fig. 5).

4. The comparison with the literature as shown in Figure 2 f should include exact references. Providing them on-site should be the responsibility of the authors and not left to the reader to pinpoint which of the references cited in the text corresponds to a given dataset.

Response: We sincerely thank the reviewer for this insightful suggestion. We fully agree that precise and transparent attribution of literature data is essential for clarity and reproducibility. In response to this suggestion, we have revised Fig. 2f to explicitly label each literature dataset with its corresponding reference number (see Fig. 3). Additionally, we have reviewed the entire manuscript and corrected similar issues in other figures where literature comparisons are presented (see Fig. 4). These improvements ensure that readers can directly associate each comparative data point with its original source without ambiguity. We appreciate the reviewer's recommendation and believe this change enhances the scientific rigor and readability of the manuscript.

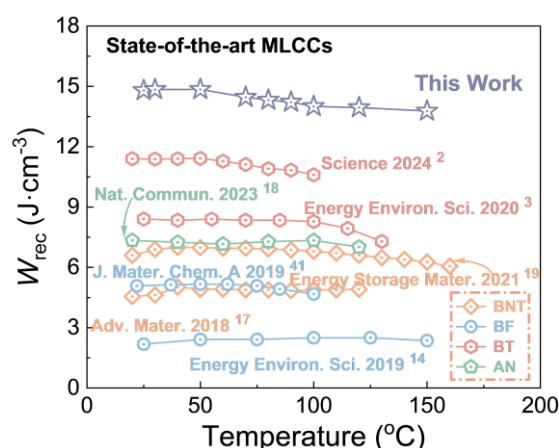


Fig. 3 Comparison of recoverable energy density across a wide operating temperature range between our study and other reported state-of-the-art MLCCs (original Fig. 2f).

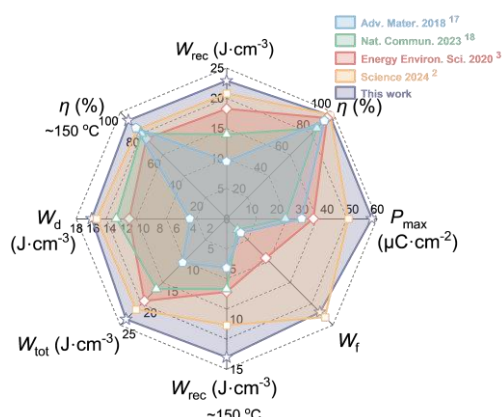


Fig. 4 Comparisons of comprehensive properties between our study and other representative MLCCs exhibiting excellent overall energy storage performance (original Fig. 2i).

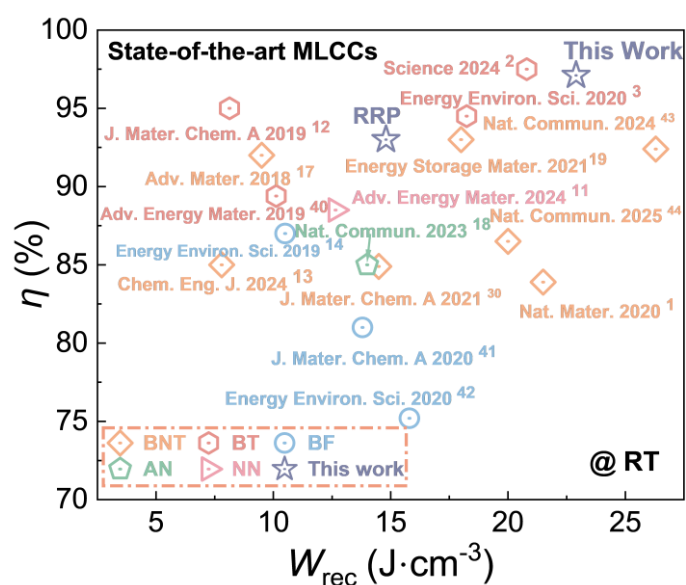


Fig. 5 Comparisons of W_{rec} and η between our work (including 1.88R-RRP) with the state-of-the-art lead-free MLCCs at room temperature (Supplementary Fig. 8).

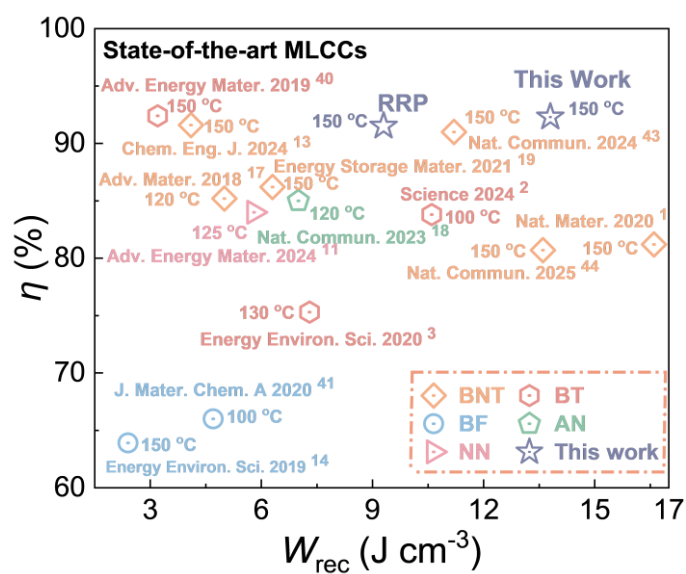


Fig. 6 Comparisons of W_{rec} versus η (100 ~ 150 °C) between our work (including 1.88R-RRP) with the most recently reported lead-free MLCCs (Supplementary Fig. 11).

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors revised the manuscript, but it is not in a better shape for readers to understand their work more clearly. However, there are still some critical issues that need to be resolved before the final decision.

Response: We sincerely appreciate the reviewer's continued evaluation of our work and the constructive feedback provided. In response to the critical points raised, we have made further improvements in both the content and clarity of the manuscript.

1. It seems that the title does not convey the information on their detail experimental results.

Response: We sincerely appreciate the reviewer's constructive comment regarding the manuscript title. We originally selected the title "*Advanced stability and energy storage capacity in hierarchically engineered ferroelectric capacitors*" to emphasize the conceptual framework and broader relevance of our study. Specifically, the phrase "*hierarchically engineered*" reflects our multiscale design strategy involving compositional tuning, microstructural control, and device-level optimization, while "*advanced stability and energy storage capacity*" succinctly summarizes the key performance outcomes.

We would also like to note that:

(1) Alignment with journal style: Titles in *Nature Communications* are typically designed to highlight general conceptual advances rather than exhaustive technical detail. Our original title follows this convention to ensure accessibility and alignment with the journal's style.

(2) Clarity without over-specification: The detailed compositional system, experimental methodologies, and performance metrics are all thoroughly detailed in the abstract, main text, and figures. Thus, while the title remains general, the full scope of the experimental content is readily accessible to interested readers.

That said, we fully acknowledge the reviewer's suggestion to make the material system more visible from the outset. In response, we have revised the manuscript title to:

“Advanced stability and energy storage capacity in hierarchically engineered $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based multilayer ceramic capacitors”

This updated version retains the original conceptual emphasis while making the material system and device architecture explicit. We believe this revision improves the manuscript's clarity and accessibility without sacrificing its broader relevance.

Thank you again for your insightful feedback, which has helped us improve the quality and presentation of our work.

2. The energy storage performance is strongly dependent on the density. What is the density of MLCC and bulk sample for different experimental conditions, such as different calcined temperature and sintering temperatures?

Response: We sincerely thank the reviewer for raising this important point. We agree that the density of dielectric ceramics plays a critical role in determining their energy storage behavior.

First, regarding the **MLCC samples**, we acknowledge the reviewer's interest in density measurement. However, we would like to clarify that **due to the presence of internal Pt electrodes within the multilayer architecture, accurate determination of the overall density using conventional techniques such as Archimedes' method is not feasible**. These techniques rely on the assumption of a homogeneous and non-conductive matrix, which is violated in the presence of metallic components. The substantial density mismatch between the ceramic and electrode layers, along with complex interfacial geometries, introduces significant measurement artifacts that compromise both the accuracy and physical relevance of the results. Therefore, our density analyses and discussions primarily focus on the **bulk ceramic samples and multilayer ceramic samples without internal electrodes**, where reliable measurement is possible.

Second, for the **bulk ceramic samples**, the pre-calcination temperature was selected in the range of 800-850 °C. This temperature window was chosen primarily to ensure complete phase formation while minimizing the volatilization of volatile constituents. Specifically, if the pre-calcination temperature is too low, incomplete phase formation may occur; whereas excessively high temperatures can lead to significant volatilization of Bi, Na, and K. That said, the pre-calcination step does not directly determine the final sample density, as the powders subsequently undergo secondary ball milling, which helps re-homogenize the particles and eliminate soft agglomerates.

By contrast, the final sintering temperature is the most critical parameter for achieving densification. In this work, we found that sintering within the temperature range of 1160-1200 °C consistently resulted in effective densification. The relative density values of 1.88R bulk ceramics (1.88R-BC, with a theoretical density of 5.87 g cm⁻³) under different sintering conditions, along with the corresponding theoretical breakdown strength (E_b) derived from Weibull analysis, are summarized in Supplementary Fig. 28 (see Fig. 1). Notably, the sample sintered at 1190 °C exhibited the highest relative density (up to 98.3%), and achieved the maximum E_b under this optimized condition. Additionally, the relative densities of multilayer ceramic samples without internal electrodes (denoted as 1.88R-MLC) sintered at different temperatures have also been included in the same figure for comparison.

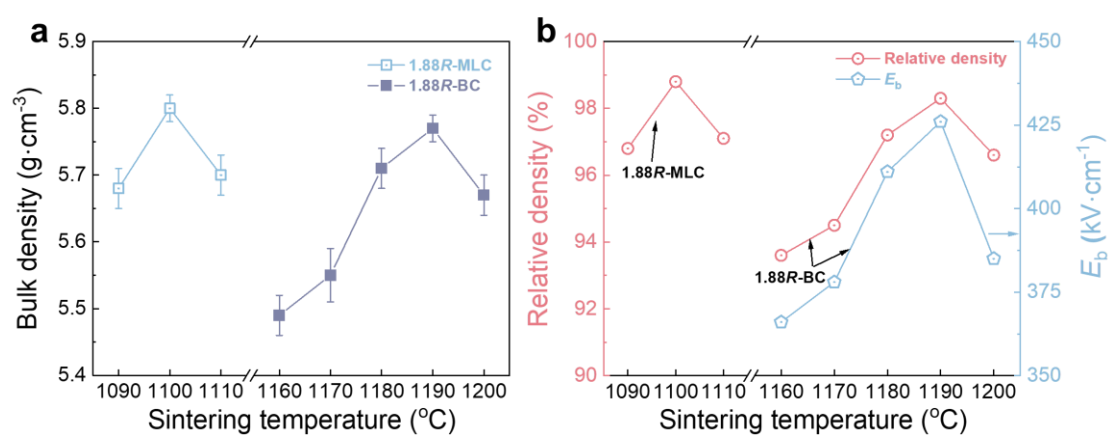


Fig.1 Effect of sintering temperature on 1.88R-MLC and 1.88R-BC. a Bulk density variation of 1.88R-MLC and 1.88R-BC with sintering temperature. **b** Relative densities

of 1.88R-MLC and 1.88R-BC and theoretical E_b of 1.88R-BC as a function of sintering temperature.

In the revised manuscript, we have explicitly included the optimal sintering temperature for 1.88R-BC to ensure the reproducibility of our results. This information, along with the detailed relative density data in Supplementary Fig. 28, should provide readers with the necessary details to understand and reproduce our experimental conditions and findings.

Reviewer #2 (Remarks to the Author):

Authors have done extensive work to resolves the doubts. It can be accepted.

Response: We express our sincere gratitude for your thorough review of our manuscript. Your insightful feedback and constructive comments have been immensely valuable in refining our work.

We believe that these changes have significantly enhanced the clarity, rigor, and overall quality of the research presented.

Once again, we sincerely thank you for your positive comments and for recommending our manuscript for publication in ***Nature Communications***. We extend our appreciation for your time and expertise in evaluating our work. Your efforts have undoubtedly played a crucial role in improving the scholarly merit of our paper.

Reviewer #3 (Remarks to the Author):

The responses of the authors and the revised manuscript provide explanations to some critical points raised in the review of the original version. There are no further comments.

Response: Thank you for reviewing our manuscript once again and for acknowledging that we have addressed your comments. We appreciate your meticulous evaluation and valuable feedback, which has undoubtedly contributed to enhancing the quality of our work. Your expertise and critical insights have been instrumental in shaping the final version of the manuscript.

Considering the thorough revisions made, we believe that the manuscript now meets the rigorous standards of the journal.

Once again, thank you for your invaluable contribution to this work.

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

Authors resolved the issues from reviewer.

Response: We sincerely thank the reviewer for the positive assessment and for recognizing that the concerns raised in the previous round have been adequately addressed. We greatly appreciate your time and thoughtful evaluation, which have contributed to improving the clarity and overall quality of our manuscript.

Small comments: 2 hours, 1h. It is better to unify the words.

Response: We thank the reviewer for the helpful comment. We have carefully reviewed the manuscript and unified all time-related expressions to the format “hours” throughout the text and figure captions to ensure consistency and clarity.