

Ultra-high energy storage in lead-free NaNbO₃-based relaxor ceramics with directional slush-like polar structures design

Corresponding Author: Professor Di Zhou

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

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I have carefully read the manuscript "Ultra-high energy storage in lead-free NaNbO₃-based relaxor ceramics with directional slush-like polar structures design". The manuscript is devoted to the study of the possibility of achieving improved energy storage performance of NaNbO₃-Bi(Mg_{0.5}Hf_{0.5})O₃ ceramics. The authors carried out phase field modelling, which helped to establish the relationship between the microstructure and the properties of the dielectric ceramics. Then, based on the modelling results, ceramic dielectrics were fabricated and their electrical properties were investigated. As a result, ceramics with high energy storage density and high efficiency were obtained. The work is original and makes a significant contribution to the development of dielectric ceramics for modern multilayer ceramic capacitors. The conclusions and statements made in the thesis are fully confirmed by the most modern research methods. It has not been possible to identify any shortcomings in the analysis of the data. The "Methods" and "Supplementary Information" sections are sufficiently detailed to allow the work to be reproduced. This manuscript has been accepted for publication in Nature Communications without further corrections.

Reviewer #2

(Remarks to the Author)

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

Fatima el bachraoui

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Responses to Reviewer # 1:

Reviewer #1 (Remarks to the Author):

Comments 1: I have carefully read the manuscript “Ultra-high energy storage in lead-free NaNbO_3 -based relaxor ceramics with directional slush-like polar structures design”. The manuscript is devoted to the study of the possibility of achieving improved energy storage performance of $\text{NaNbO}_3\text{-Bi}(\text{Mg}_{0.5}\text{Hf}_{0.5})\text{O}_3$ ceramics. The authors carried out phase field modelling, which helped to establish the relationship between the microstructure and the properties of the dielectric ceramics. Then, based on the modelling results, ceramic dielectrics were fabricated and their electrical properties were investigated. As a result, ceramics with high energy storage density and high efficiency were obtained. The work is original and makes a significant contribution to the development of dielectric ceramics for modern multilayer ceramic capacitors. The conclusions and statements made in the thesis are fully confirmed by the most modern research methods. It has not been possible to identify any shortcomings in the analysis of the data. The “Methods” and “Supplementary Information” sections are sufficiently detailed to allow the work to be reproduced. This manuscript has been accepted for publication in Nature Communications without further corrections.

Responses: We highly appreciate the positive comments for the present study.

Responses to Reviewer # 2:

Reviewer #2 (Remarks to the Author):

The authors' paper proposes a strategy for enhancing energy storage density while maintaining high efficiency. The directional slush-like polar structure in lead free multilayer ceramic capacitors (MLCCs), proposed by this group, shows a reduction of the hysteresis loss, while at the same time improves the breakdown electric field. A high energy density of 14.1 J/cm^3 and an ultrahigh energy storage efficiency of 96.8% are achieved. The directional slush-like polar structure design with nanodomains embedded in polar orthorhombic matrix in sodium niobite (NaNbO_3)-based lead-free MLCCs is a novel approach that has achieved a good balance between high energy density and efficiency. Although the high energy density obtained in this work, it is still low in comparison with Da Li et al. (16, Article number: 188 (2025) who have obtained a large energy density of 20.0 J/cm^3 along with a high efficiency of 86.5% with remarkable high temperature stability. The proposed directional slush-like polar structure strategy by the authors in comparison with the feasible routine from nano, micro to macro regions in manipulating local polarizations proposed by Da Li et al. (16, Article number: 188 (2025) for example. Therefore, the authors should consider the following questions and recommendations before accepting the manuscript:

Response: We appreciate the reviewer's comment. Although a high energy storage density of 20 J/cm^3 was obtained in the study of Da Li et al. the energy storage efficiency of 86.5% is still low. Due to the small size of the MLCC and its low heat dissipation capability, the energy loss generates a huge amount of heat, which increases its temperature significantly. It has been reported that even with 85% efficiency, the

heat generated by the energy loss ($\sim 2 \text{ J cm}^{-3}$) of an MLCC with an energy density of $\sim 15 \text{ J/cm}^3$ leads to a temperature increase of up to 200°C , which is seriously beyond the temperature range for stabilizing the energy storage performance. To limit the temperature rise below 50°C , the energy efficiency must be greater than 95% in the MLCC. Thus, near-zero energy loss becomes a prerequisite for MLCCs with high energy storage density. Here, ultra-high energy storage efficiency ($\sim 96.8\%$) accompanied by high energy storage density ($\sim 14.1 \text{ J/cm}^3$) was obtained by directional slush-like polar structure design strategy in MLCCs.

Comments 1: Do the authors see potential in their proposed strategy and methodology to obtain higher energy density than 14.1 J/cm^3 using other dopant or materials?

Response: Thank you for your comment. We believe that the proposed strategy and methodology can potentially use other dopants or materials to obtain higher energy density than 14.1 J/cm^3 because the number of O-type nanodomains can be controlled by using different dopants or materials. If other dopants can increase the number of O-type nanodomains, then theoretically the energy density will be higher than now. Similarly, Yang et al.¹ increased the number of O-type nanodomains to achieve a record high energy density of 189 J/cm^3 and high efficiency of 81% via an antipolar frustration strategy in the $0.8\text{PbZr}_{0.925}\text{Hf}_{0.075}\text{O}_3\text{-}0.2\text{LaScO}_3$ film. In addition, we believe that this strategy can be applied to other antiferroelectric material systems such as AgNbO_3 , PbZrO_3 , PbHfO_3 and so on.

The references are as follow:

- [1] Yang, B. et al. Enhanced energy storage in antiferroelectrics via antipolar frustration. *Nature* **637**, 1104–1110 (2025).

Comments 2: Could the authors please clarify the following: Bi(Mg_{0.5}Hf_{0.5})O₃ is used as the guest phase for polarization direction disorder, what specific properties of this guest that that contributes to the directional alignment of nanodomains? And is this approach is valid for all dopants? or it is specific to only Bi(Mg_{0.5}Hf_{0.5})O₃?

Response: Thank you for your valuable suggestion. We apologize for the clerical error in the last paragraph of the introduction: “guest phase Bi(Mg_{0.5}Hf_{0.5})O₃” should have been changed to “guest phase Bi(Ni_{0.5}Hf_{0.5})O₃”. In the NaNbO₃-based system, we believe that the decrease in the tolerance factor favors the directional alignment of the nanodomains due to the doping of the guest phase. Tolerance factor (t) is calculated as follows: $t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$, where R_A , R_B , and R_O are the ionic radii of the A-site, B-site, and O-site, respectively^{1,2}. On the one hand, when the doping content is low, the oriented antiferroelectric domains will be stabilized as the tolerance factor decreases; On the other hand, when the doping content is high, the doping of the guest phase will break this long-range ordered oriented antiferroelectric domains, which in turn will form an oriented arrangement of nanodomains. We believe that this method is suitable for systems with a reduced tolerance factor with the doping of the guest phase. In this study, the tolerance factor of NaNbO₃ is 0.974 while that of Bi(Ni_{0.5}Hf_{0.5})O₃ is 0.821 according to Shannon’s ionic radius data (<http://abulafia.mt.ic.ac.uk/shannon/ptable.php>), so the tolerance factor of the system

decreases. We believe that the following guest phases are also suitable for this method, e.g. $\text{Bi}(\text{Mg}_{0.5}\text{Hf}_{0.5})\text{O}_3$ ($t=0.815$), $\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$ ($t=0.813$), etc.

The references are as follow:

- [1] Luo, N. et al. Well-defined double hysteresis loop in NaNbO_3 antiferroelectrics. *Nat. Commun.* **14**, 1776 (2023).
- [2] Zhao, L. et al. Lead-free antiferroelectric silver niobate tantalate with high energy storage performance. *Adv. Mater.* **29**, 1701824 (2017).

Comments 3: Over the long operation, do the embedded nanodomains remain stable under repeated electric field? Did the authors predict any coarsening of these nano - domains in long term operation?

Response: We appreciate the reviewer's comment. We consider that the embedded nanodomains remain essentially stabilized under repeated electric fields. In terms of microstructure, the nanodomains range in size from 1 nm to 3 nm, and nanodomains with lower energy barriers can rapidly flip under repeated applied electric fields. In terms of macroscopic performance, $x = 0.15$ (MLCC) exhibits a small performance deterioration ($\Delta W_{\text{rec}} \sim 2\%$, $\Delta \eta \sim 1\%$) after 10^5 cycles. Therefore, we speculate that these nanodomains are coarsened to some extent during long-term operation, but not significantly. Anyway, thank the reviewer for the valuable comment and we will further verify this phenomenon in our future work.

Comments 4: Can the authors please explain how was the alignment of nanodomains quantified?

Response: Thank you for your valuable suggestion. The alignment of the nanodomains

can be quantified by the polarization displacement size distribution and vector angle distribution histograms as shown in Fig. R1 (Supplementary Fig. 12). The average displacement of polarization is about 19.3 pm (Fig. R1a), which is conducive to obtaining high maximum polarization. The vector angular distribution plot (Fig. R1b) shows that the polarization vector is 88.3% in the range of 0-120°, which is much higher than the 11.7% in the other angular ranges (120-360°) and is therefore defined as a directional slush-like polar structure. The figure has been added to the Supplementary Information (Fig. S12) and the relevant discussions have been added to the manuscript.

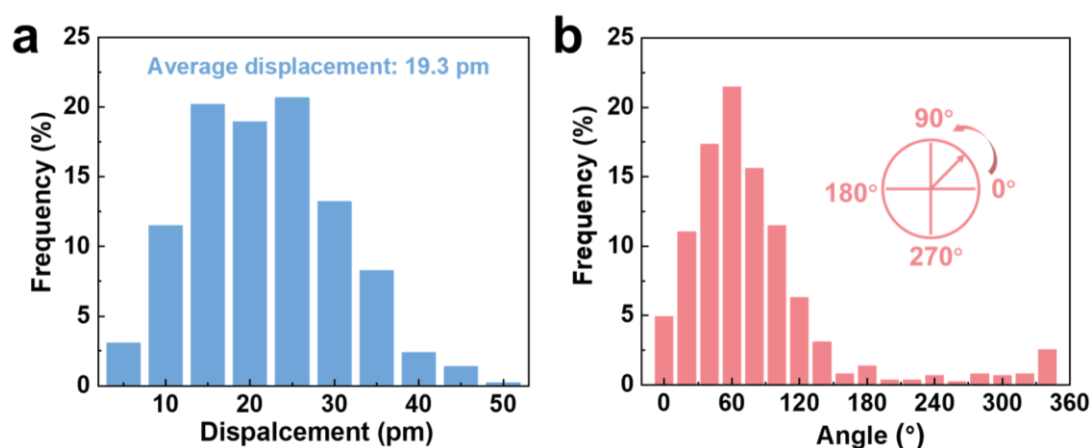


Fig. R1 (Supplementary Fig. 12) **a** Displacement magnitude distribution and **b** Vector angle distribution histogram of the $x=0.15$ ceramic.

Comments 5: Can the authors explain why the thermal stability tests are not tested at 200 °C or 250 °C and were satisfied at 150 °C? What are the limitations of the DSP structure at temperatures above 150 °C?

Response: Thank you for your comment. In general, thermal stability testing to 150 °C has met the needs of most high-temperature ceramic capacitors, for example, the X7R type capacitor has a maximum operating temperature of 125 °C. Besides, the silicone

oil used for our ferroelectric tester can only stand up to 150 °C, above which silicone oil volatilizes seriously. As you have stated, the increasing demand for ultra-high operating temperatures ($\geq 200^{\circ}\text{C}$) with the continuous development of electronic information will push us to achieve higher operating temperatures in multilayer ceramic capacitors. Possible component temperature phase diagrams were plotted and shown in Fig. R2 via dielectric temperature spectrum data. For $x = 0.15$ ceramics, the highest possible temperature at which the DSP structure can exist is approximately 253 °C, while the DSP structure will transition to the paraelectric state with further temperature increase ($>253^{\circ}\text{C}$).

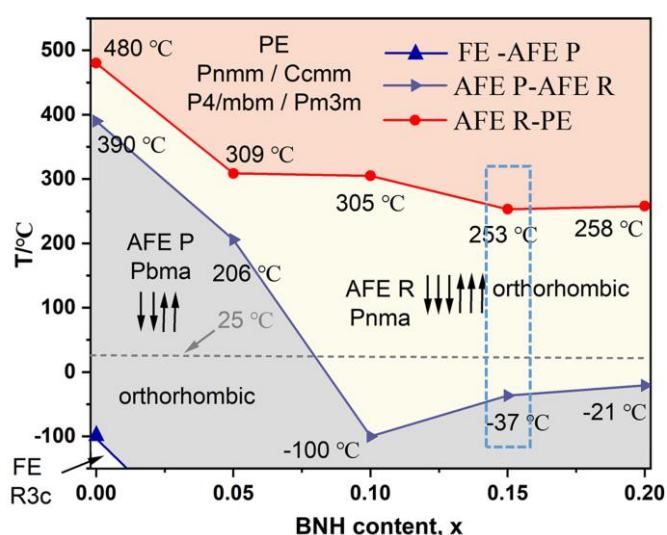


Fig. R2 Possible composition temperature phase diagram of $(1-x)$ NN- x BNH solid solution with x from 0 to 0.20.

Comments 6: Similar to frequency, why the stability test is limited to 100 Hz and not higher? Does high frequency influence the response of the material?

Response: We appreciate the reviewer's comment. In general, frequency stability testing to 100 Hz has met the needs of most ceramic capacitors, as reported in most of

the literature¹⁻³. As you say, higher frequency stability testing (>100 Hz) may be needed in practical applications in the future. The test frequency affects the response of the material. The hysteresis loss (W_{loss}) with change in frequency is provided in Fig. R3. The nanodomains flip with the change in electric field, and the flip is accompanied by domain wall motion. As the test frequency increases, the flip period of the electric field decreases, and a part of the nanodomains cannot flip, showing a decrease in the residual polarization, leading to a decrease in the W_{loss} . In addition, the domain wall motion during nanodomain flip is resisted by viscous-like forces between the nanodomains, and this resistance increases with the frequency, making a larger electric field required for a complete flip of the nanodomains, exhibiting an increase in the coercive field and leading to a further increase in W_{loss} . This figure has been added to the Support Information (Fig. S6) while these descriptions have been added to the discussion section on energy storage stability.

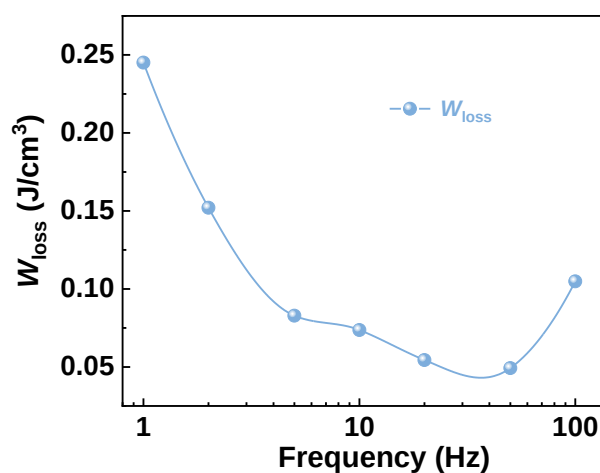


Fig. R3 (Supplementary Fig. 6) Hysteresis loss (W_{loss}) change with frequency (1-100 Hz) for $x=0.15$ (MLCC) at 720 kV/cm.

The references are as follow:

[1] Zhu, L. et al. Heterovalent-doping-enabled atom-displacement fluctuation leads to

ultrahigh energy-storage density in AgNbO₃-based multilayer capacitors. *Nat. Commun.* **14**, 1166 (2023).

- [2] Yan, F. et al. Tape-casting lead-free dielectrics permit superior capacitive energy storage performance. *Adv. Energy Mater.* doi:10.1002/aenm.202403535 (2024).
- [3] Luo, H. et al. Outstanding energy-storage density together with efficiency of above 90% via local structure design. *J. Am. Chem. Soc.* **146**, 1 (2024).

Comments 7: The NMR was used to characterize the structural distortion to the NaO₁₂ cuboctahedra, and isotropic chemical shifts (δ_{iso}) were used to express the average Na-O distances. The results show that C_Q value decreases from 1043 kHz to 813 kHz, and an increase in the Na-O bond distance is observed. How do these changes quantitatively influence the dielectric and ferroelectric properties of the material?

Response: We thank the reviewer for their careful review of the NMR data. The analysis of C_Q and δ_{iso} did provide valuable insights into the characterization of the present sodium species. The variation of NMR parameters (C_Q and δ_{iso}), dielectric properties (γ) and ferroelectric properties (W_{rec}) with components is provided in Fig. R4. As can be seen from the figure, there is a substantial increase in both γ and W_{rec} of the material with decreasing C_Q and δ_{iso} for $x=0$ and $x=0.15$ ceramics, this is in agreement with the results of the NMR study by Zhang et al.¹ (The relaxation properties of the material are enhanced and W_{rec} increases by almost 14 times with decreasing C_Q and δ_{iso} in $(1-x)\text{NaNbO}_3-x\text{SrSnO}_3$ ceramics), suggesting that more disordered localized structures possessing smaller distortions at the Na(1) site are favorable for energy storage performance. The figure is provided in the Support Information (Fig. S14) while

“As C_Q and δ_{iso} decrease, both γ and W_{rec} of the material increase substantially for $x=0$

and $x=0.15$ ceramics (Fig. S14), which agrees with most NMR results for relaxing perovskite oxides possessing disordered localized structures^{17,31}, further demonstrating that $x=0.15$ component is indeed in a relaxed state, suggesting that more disordered localized structures possessing smaller distortions at the Na(1) site are favorable for energy storage performance.” has been added to the manuscript.

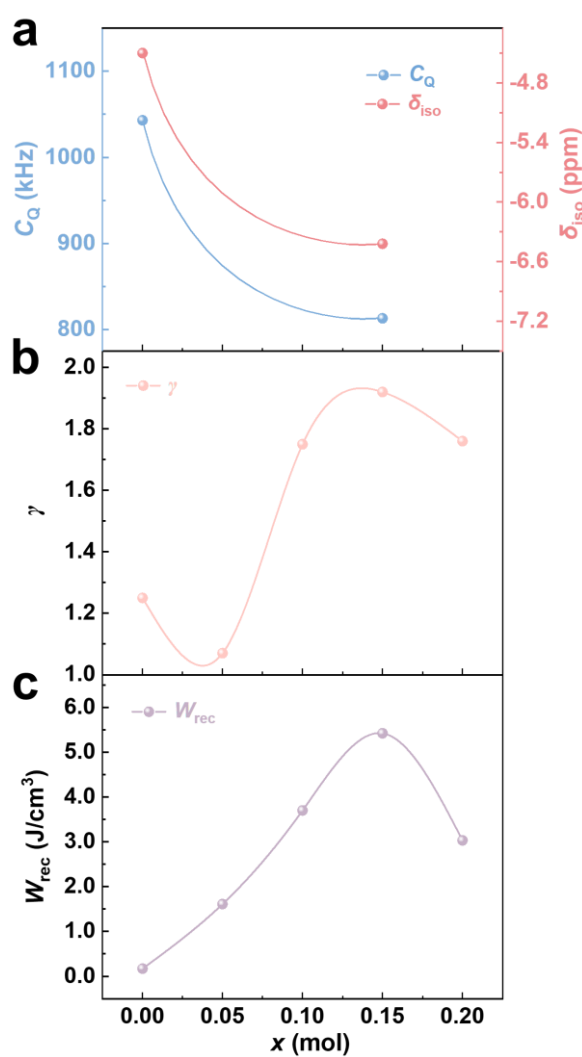


Fig. R4 (Supplementary Fig. 14) **a** C_Q and δ_{iso} , **b** relaxor diffuseness factor γ , **c** discharge energy density W_{rec} change with x for $(1-x)\text{NN}-x\text{BNH}$ ceramics.

The references are as follow:

- [1] Zhang, M. *et al.* Tailoring high-energy storage NaNbO_3 -based materials from antiferroelectric to relaxor states. *Nat. Commun.* **14**, 1525 (2023).

Responses to Reviewer # 1:

Reviewer #1 (Remarks to the Author):

Comments 1: After thoroughly reviewing the authors' responses, the reviewer is satisfied that all questions and concerns have been addressed comprehensively and with careful consideration. The manuscript titled "Ultra-high energy storage in lead-free NaNbO₃-based relaxor ceramics with directional slush-like polar structures design" has met the necessary standards and is deemed ready for publication. The reviewer expresses appreciation to the authors for their detailed explanations and insightful discussion, which have enhanced the clarity and robustness of the manuscript. Thank you for your diligent efforts in responding to the feedback.

Responses: We highly appreciate the positive comments for the present study.

Manuscript Title:

Ultra-high energy storage in lead-free NaNbO₃-based relaxor ceramics with directional slush-like polar structures design.

Comments to authors:

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