

Supplementary Information

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

Zhentaο Wang¹, Da Li¹, Wenyuan Liu², Liqiang He^{3*}, Diming Xu^{1*}, Jinnan Liu¹, Jiajia Ren¹, Xin Wang¹, Yang Liu¹, Guoqiang He¹, Jian Bao¹, Zhen Fang¹, Guiwei Yan¹, Xu Liang², Tao Zhou⁴, Weichen Zhao^{1*}, Wenfeng Liu⁵, Dong Wang^{3*} and Di Zhou^{1*}

¹ Multifunctional Materials and Structures, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China

² State Key Laboratory for Strength and Vibration of Mechanical Structures, School of Aerospace Engineering, Xi'an Jiaotong University, Xi'an 710049, China

³ State Key Laboratory for Mechanical Behavior of Materials, Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an 710049, China

⁴ School of Electronic and Information Engineering, Hangzhou Dianzi University, Hangzhou 310018, China

⁵ State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, China

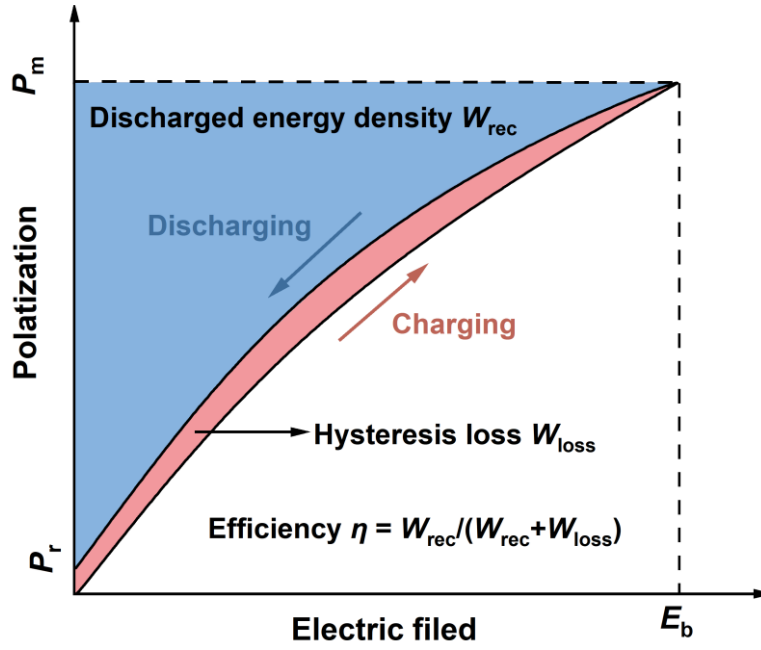
* Corresponding author: Liqiang He; E-mail address: heliqiang0818@xjtu.edu.cn

* Corresponding author: Diming Xu; E-mail address: diming.xu@xjtu.edu.cn

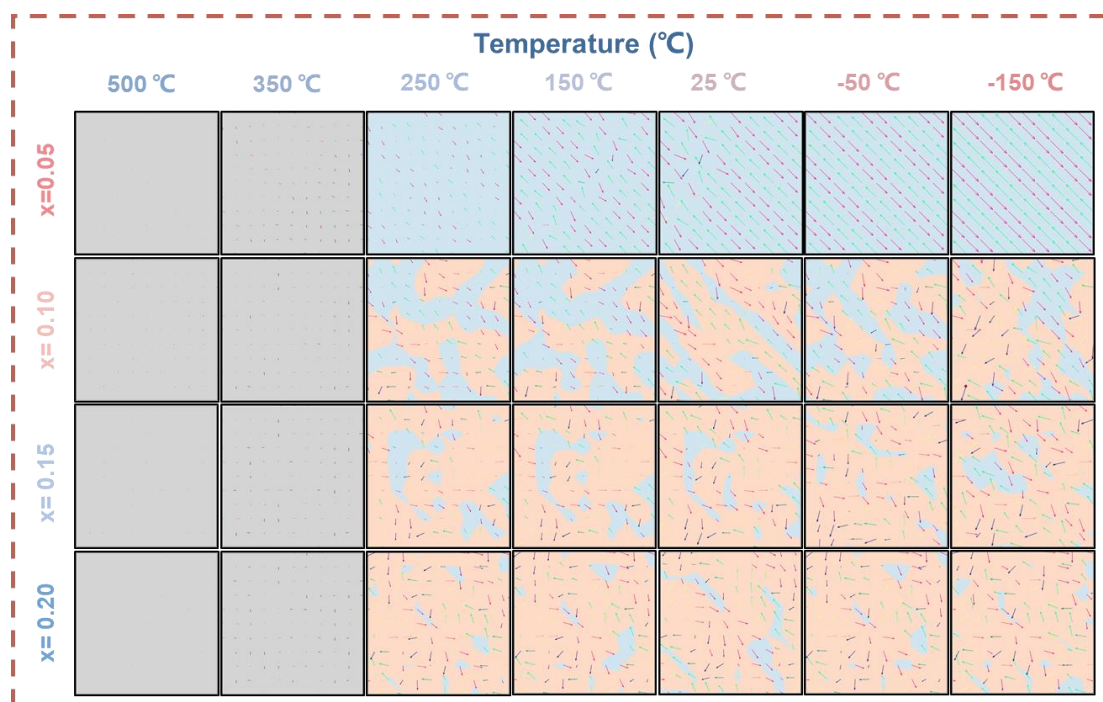
* Corresponding author: Weichen Zhao; E-mail address: zhaoweichen@stu.xjtu.edu.cn

* Corresponding author: Dong Wang; E-mail address: wang_dong1223@mail.xjtu.edu.cn

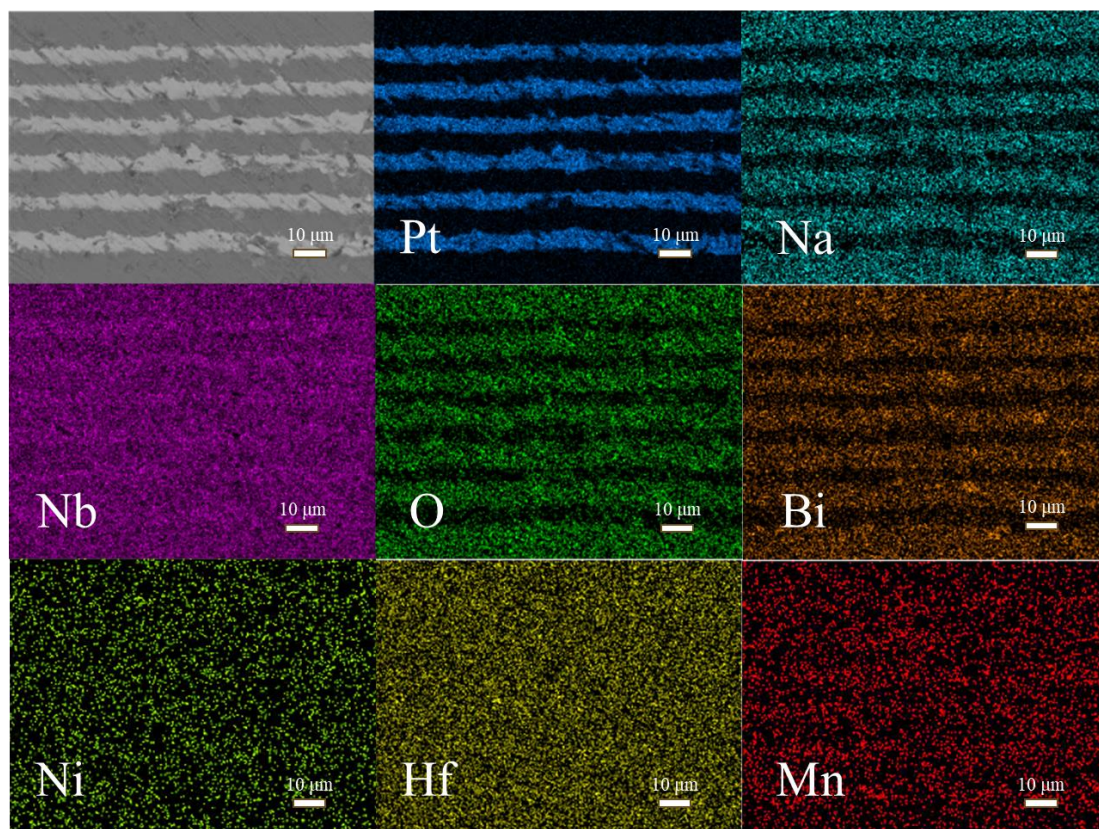
* Corresponding author: Di Zhou; E-mail address: zhoudi1220@xjtu.edu.cn



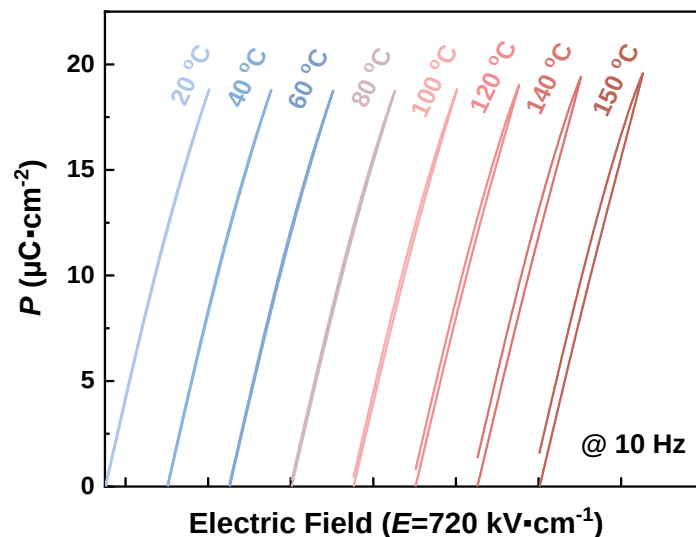
Supplementary Fig. 1 Schematic illustration of dielectric energy storage. In the charging process of a dielectric capacitor, the dielectric material is polarized, which allows for the storage of electrostatic energy. In the discharging process, the polarization is released and the stored energy is discharged. The discharged energy density (W_{rec}) can be calculated by the formula of $W_{rec} = \int_{P_r}^{P_m} E dP$ as represent by the blue area, where P_m and P_r are the maximum polarization and remnant polarization, respectively. The red area represents the energy loss W_{loss} in the charging-discharging cycle. The energy efficiency η of the dielectric is defined as $W_{rec} / (W_{rec} + W_{loss})$. E_b is the breakdown strength.



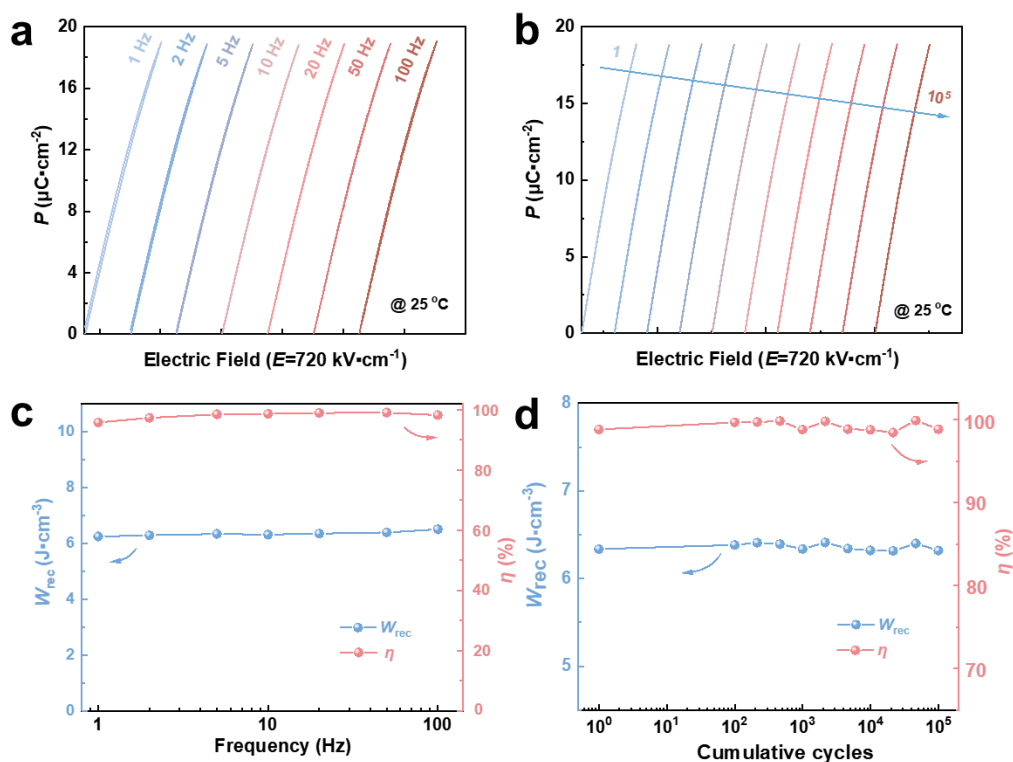
Supplementary Fig. 2 Calculated microstructural evolution of $(1-x)\text{NN}-x\text{BNH}$ system upon cooling. The blue color represents the antiferroelectric domain, and yellow color denotes the non-antiferroelectric domain, and gray color signifies the paraelectric phase.



Supplementary Fig. 3 SEM micrographs of cross-section area with elements mapping in NN-based MLCCs of $x=0.15$ (MLCC). The MLCCs shows a good quality interface between the dielectric layer (Na, Nb, O, Bi, Ni, Hf elements) and the electrode layer (Pt elements).

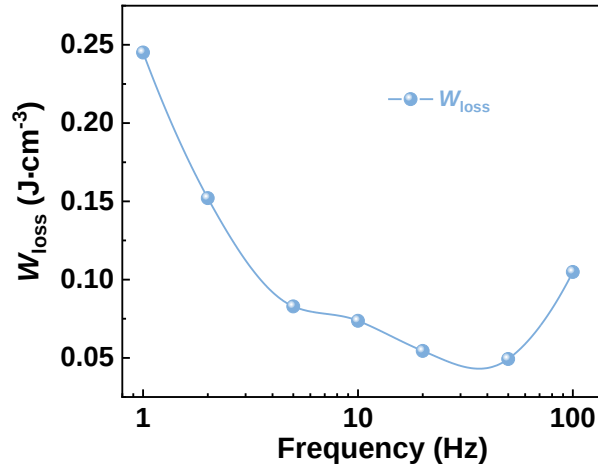


Supplementary Fig. 4 Temperature-dependent P - E loop of $x=0.15$ (MLCC) at 720 $\text{kV}\cdot\text{cm}^{-1}$.

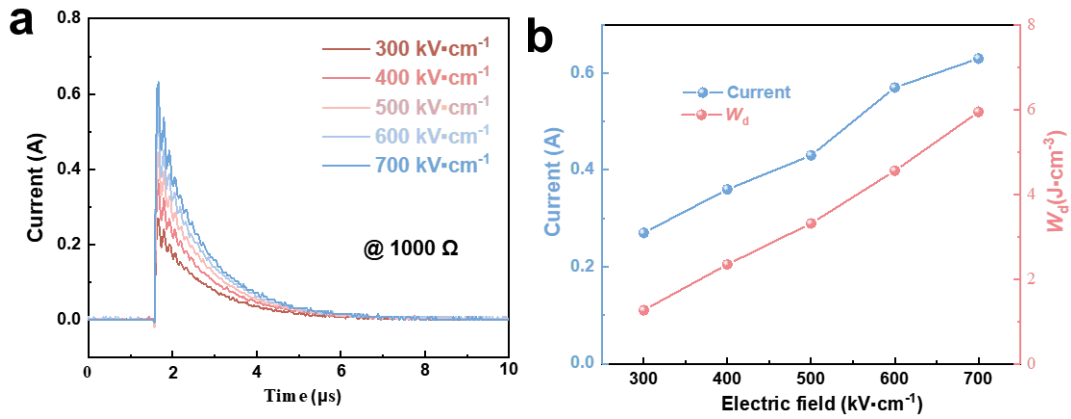


Supplementary Fig. 5 Energy storage performance of $x=0.15$ (MLCC) under different conditions. a Frequency-dependence **b** cycling-dependence P - E loops at 720

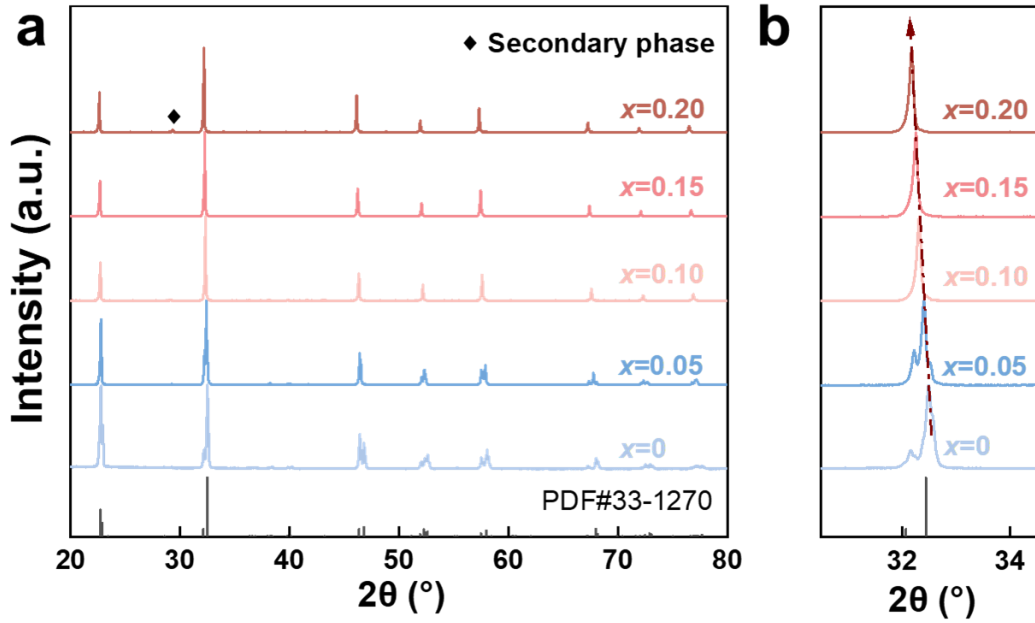
$\text{kV}\cdot\text{cm}^{-1}$. **c** W_{rec} and η of as a function of frequency **d** W_{rec} and η of as a function of the cycle number at $720 \text{ kV}\cdot\text{cm}^{-1}$.



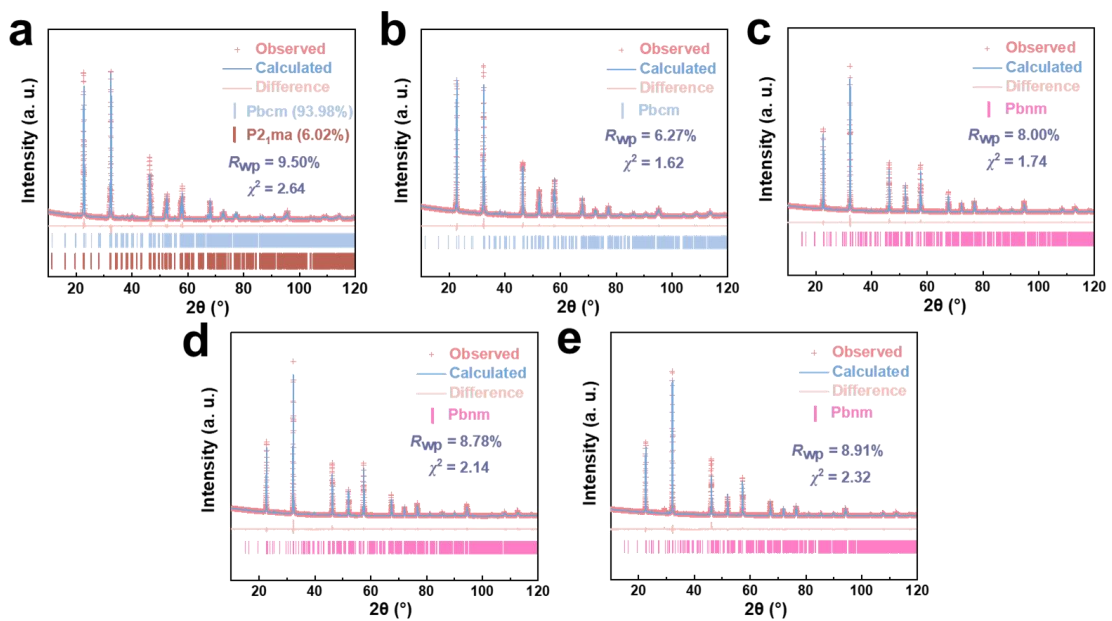
Supplementary Fig. 6 Hysteresis loss (W_{loss}) change with frequency (1-100 Hz) for $x=0.15$ (MLCC) at $720 \text{ kV}\cdot\text{cm}^{-1}$.



Supplementary Fig. 7 Actual charge and discharge performance of $x=0.15$ (MLCC). **a** Overdamped discharge waveforms wave forms at various electric fields. **b** variation of I_{max} and W_d under different electric fields.

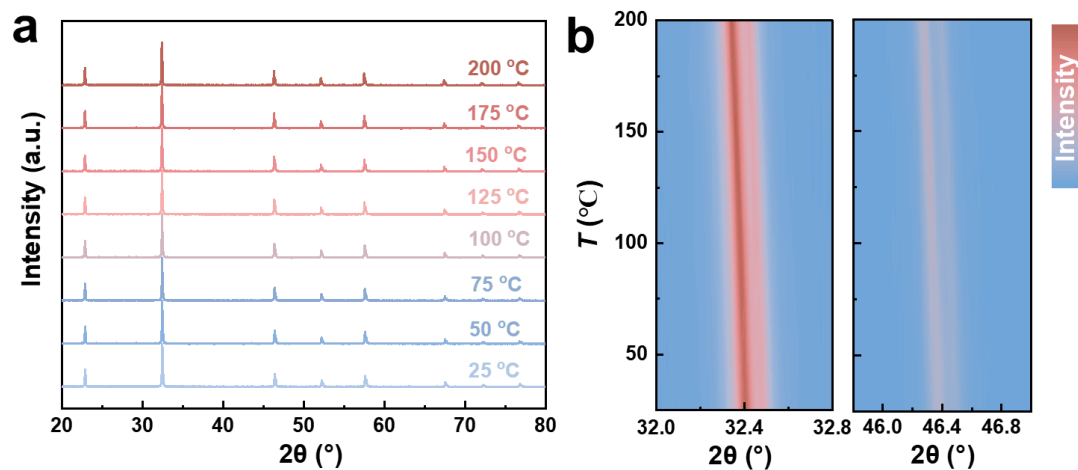


Supplementary Fig. 8 **a** XRD patterns of pure NN and (1-x)NN-xBNH ceramics. **b** enlarged view of the 2θ range of $30.5\text{--}34.5^\circ$. By expanding the XRD patterns within the 2θ range of $30.5\text{--}34.5^\circ$ for each component, as shown in Supplementary Fig. 6b, it becomes evident that the diffraction peaks gradually shift to lower 2θ angles with an increase in BNH content, suggesting an increase in cell parameters. This trend may result from the substitution of Na^+ (ionic radius = $1.39 \text{ \AA}$) by the larger Bi^{3+} ions (ionic radius = $1.45 \text{ \AA}$) at the A-site, as well as the substitution on the B-site, where the ionic radii of Ni^{2+} ($0.69 \text{ \AA}$) and Hf^{4+} ($0.76 \text{ \AA}$) are both larger than that of Nb^{5+} ($0.64 \text{ \AA}$).

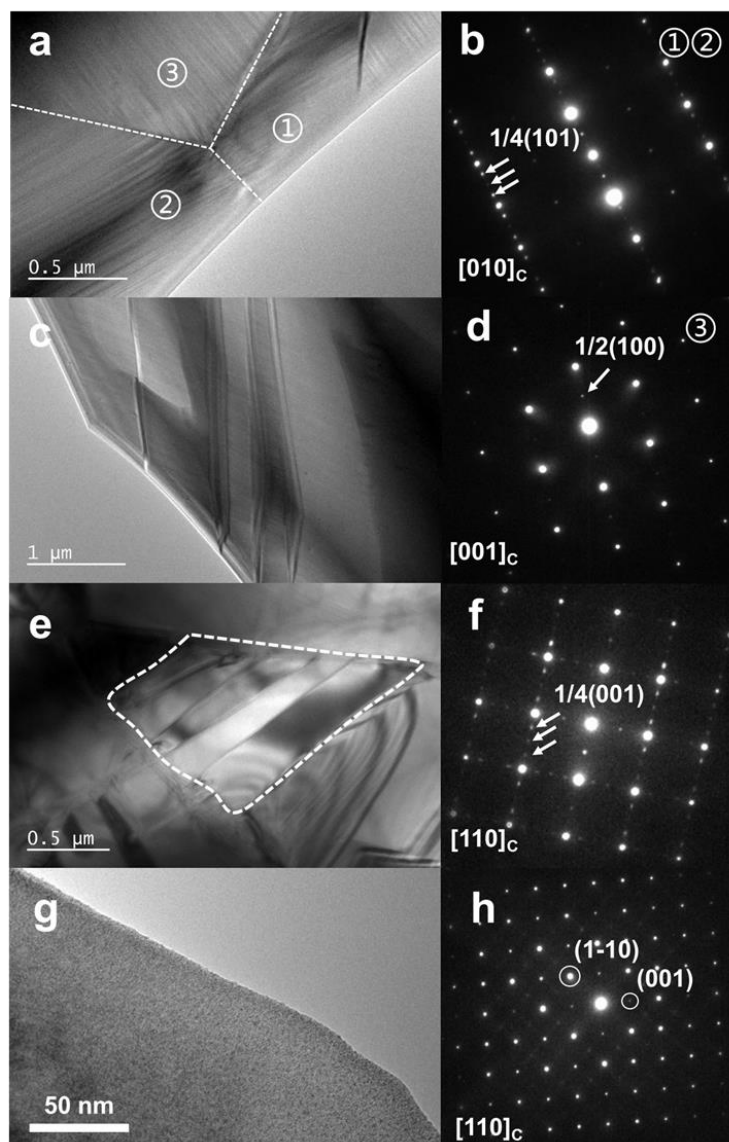


Supplementary Fig. 9 The Rietveld refinement of XRD data for the **a** $x=0$, **b** $x=0.05$,

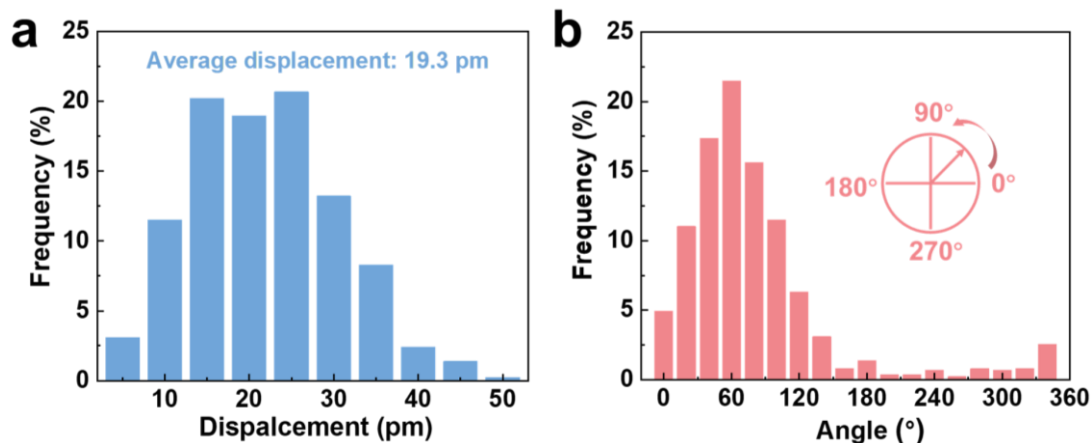
c $x=0.10$, **d** $x=0.15$ and **e** $x=0.20$ ceramics.



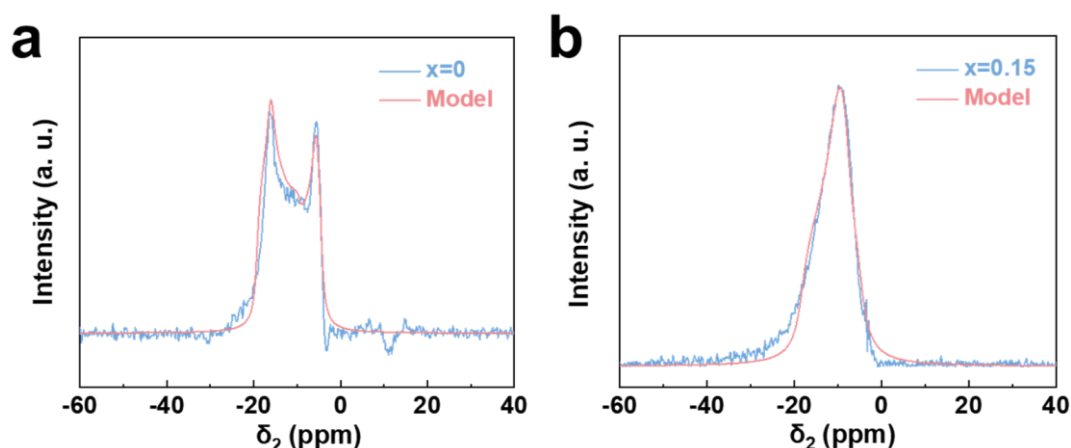
Supplementary Fig. 10 **a** Temperature-dependent XRD patterns of the $x=0.15$ ceramic from 25 to 200 °C. **b** Local magnification of XRD pattern at 32-32.8° and 45.8-47°.



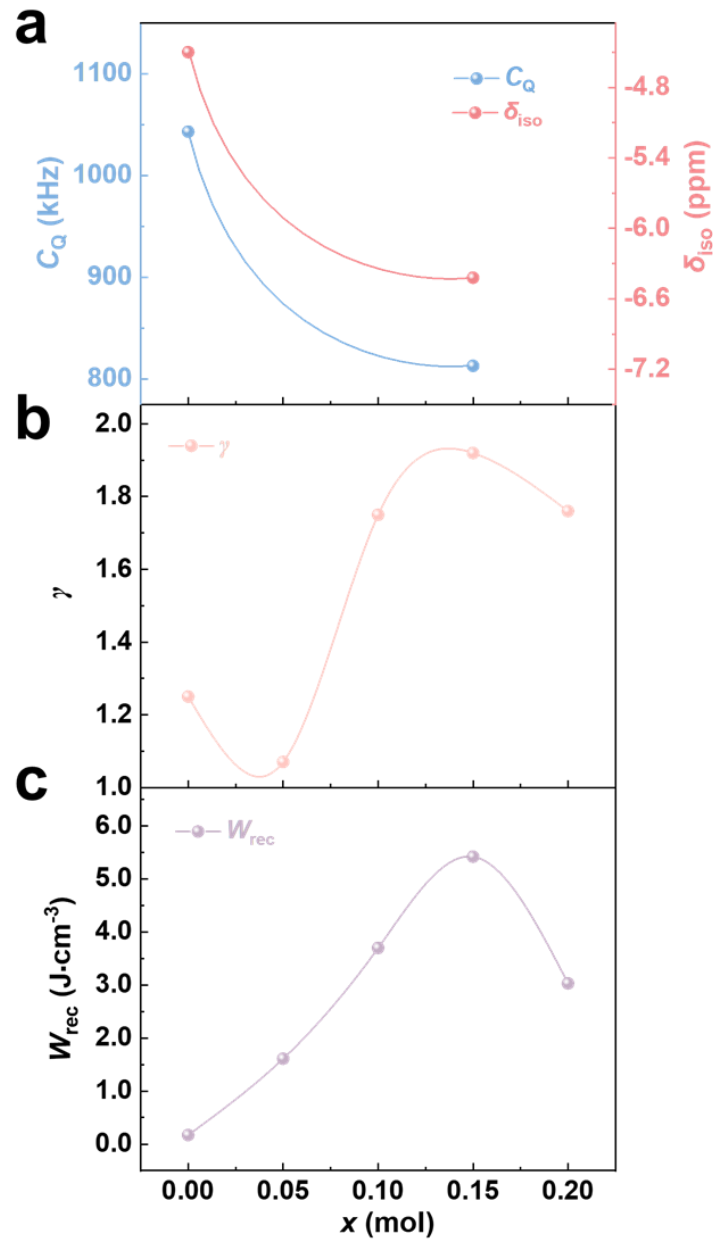
Supplementary Fig. 11 TEM images of $x=0$, $x=0.05$ and $x=0.15$ ceramics. **a** Overview bright-field image showing three domains in $x=0$ ceramics. **b** and **d** SAED patterns taken from the domains labeled (①–③) in (a). **c** Overview bright-field image in $x=0$ ceramics. **e** Overview bright-field image in $x=0.05$ ceramics. **f** SAED patterns in (e). **g** Overview bright-field image in $x=0.15$ ceramics. **h** SAED patterns in (g).



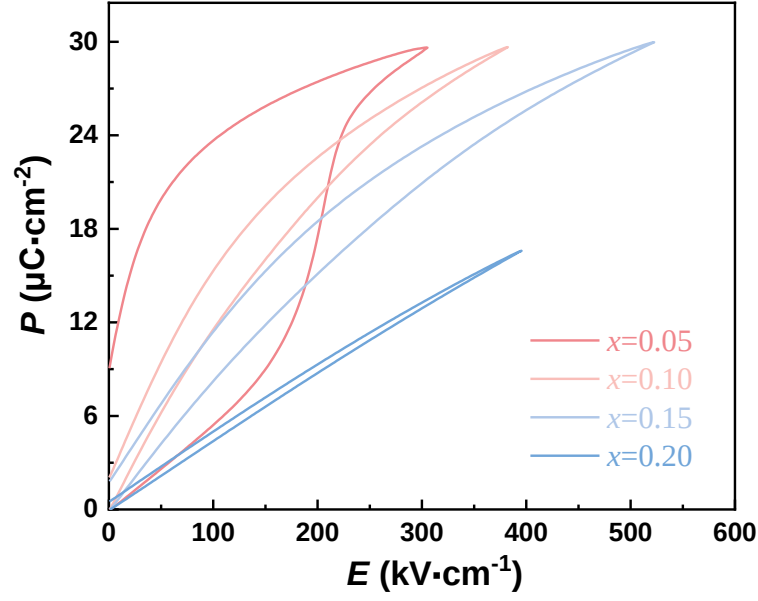
Supplementary Fig.12 a Displacement magnitude distribution and **b** Vector angle distribution histogram of the $x=0.15$ ceramic. The average displacement of polarization is about 19.3 pm, which is conducive to obtaining high maximum polarization. The vector angular distribution plot shows that the polarization 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°).



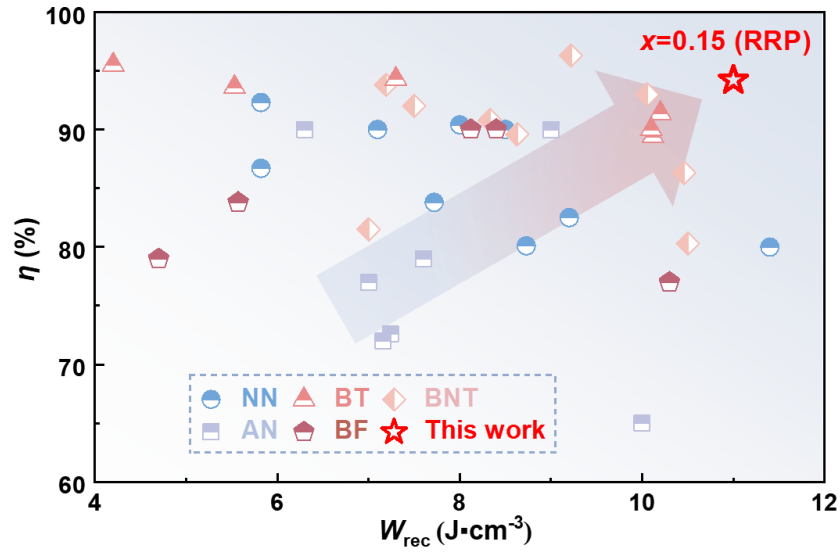
Supplementary Fig. 13 NMR fitting spectra along δ_2 . Line shape simulation of **a** $x=0$, **b** $x=0.15$, yielding the parameters reported in Supplementary Table 1.



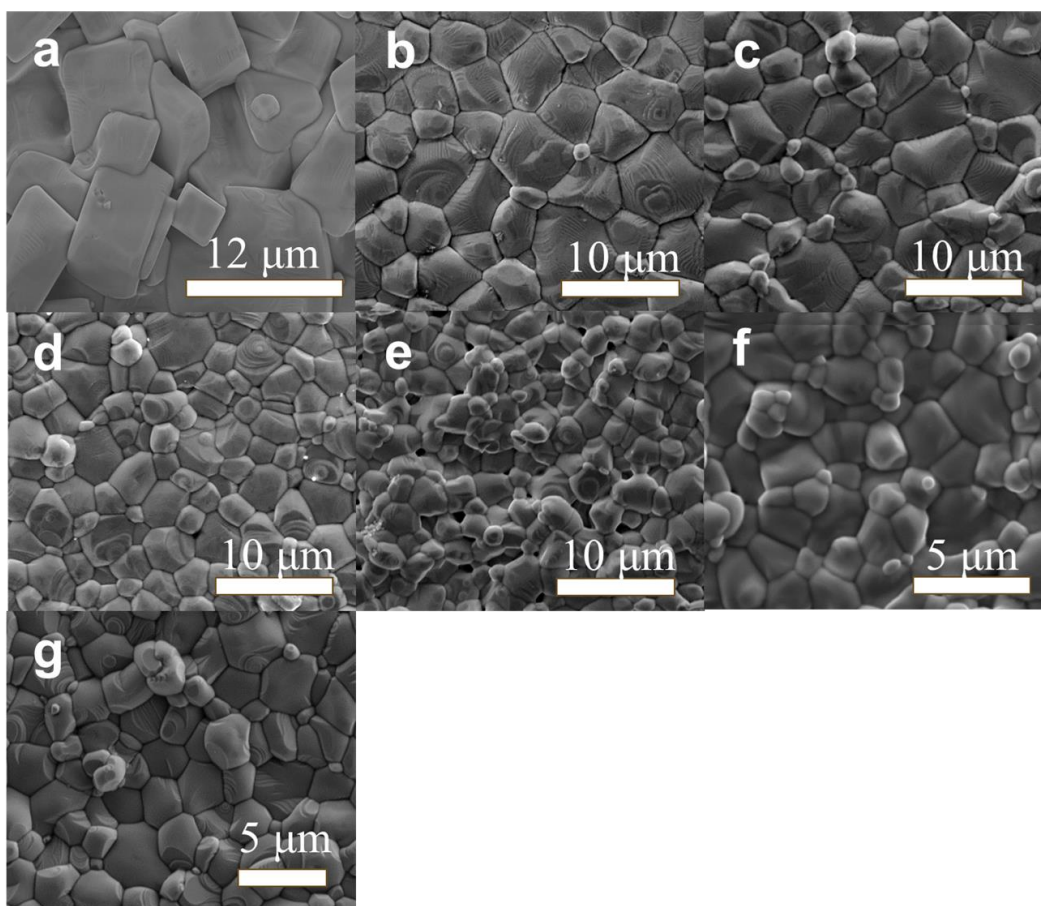
Supplementary Fig. 14 **a** C_Q and δ_{iso} , **b** relaxor diffuseness factor γ , **c** discharge energy density W_{rec} change with x for $(1-x)NN$ - $xBNH$ ceramics.



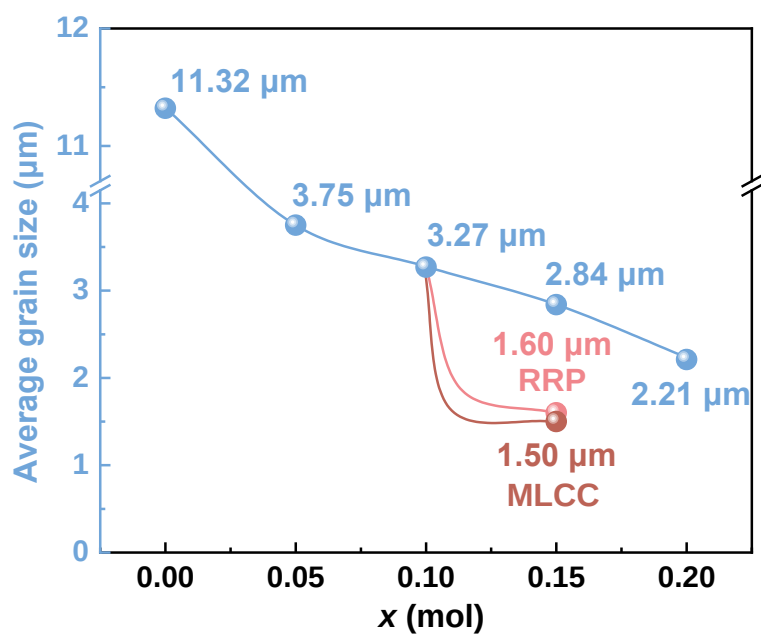
Supplementary Fig. 15 Unipolar P - E loops of $(1-x)\text{NN}-x\text{BNH}$ ceramics as a function of electric field up to E_b at 10 Hz.



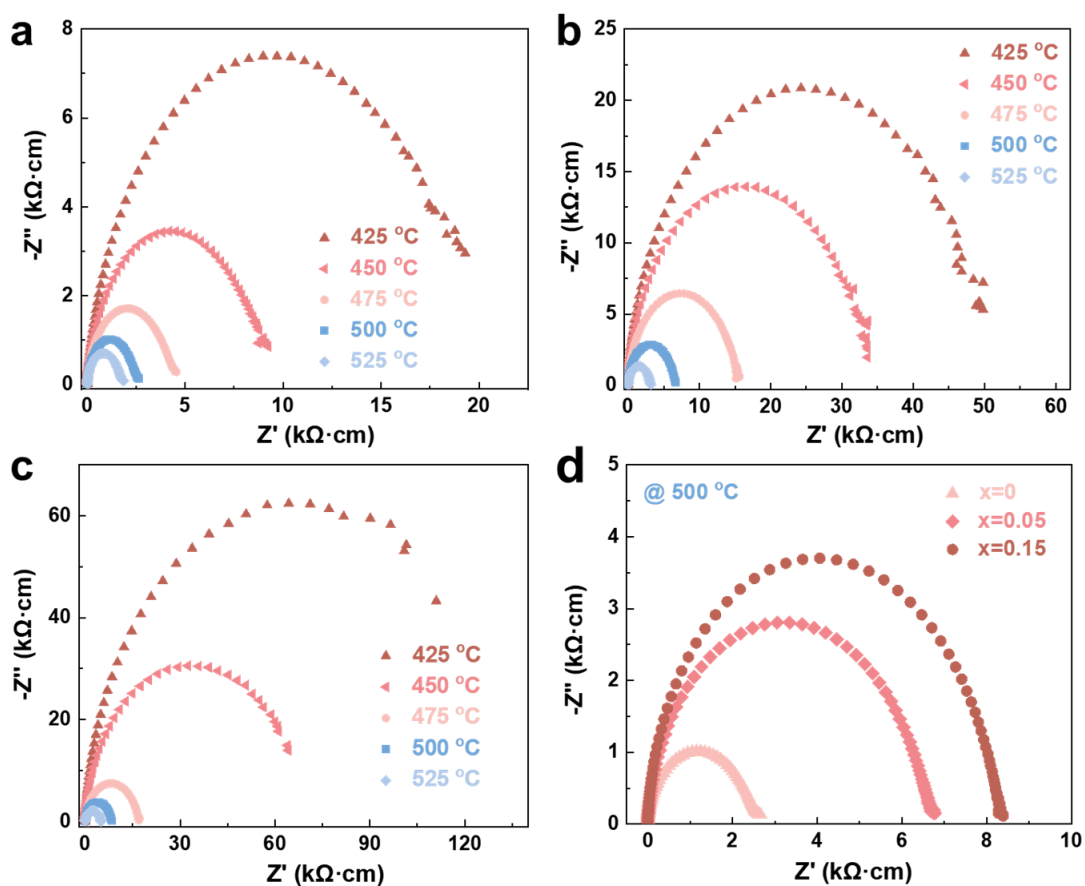
Supplementary Fig. 16 A comparison of the energy storage properties of the $x=0.15$ (RRP) and the state-of-the-art energy storage lead-free bulk ceramics.



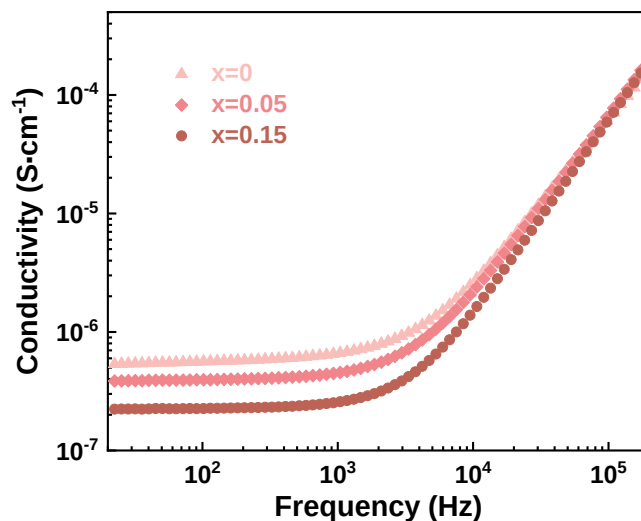
Supplementary Fig. 17 SEM micrographs of $(1-x)\text{NN}-x\text{BNH}$ ceramics. a $x=0$, b $x=0.05$, c $x=0.10$, d $x=0.15$, e $x=0.20$, f $x=0.15$ (RRP) and g $x=0.15$ (MLCC).



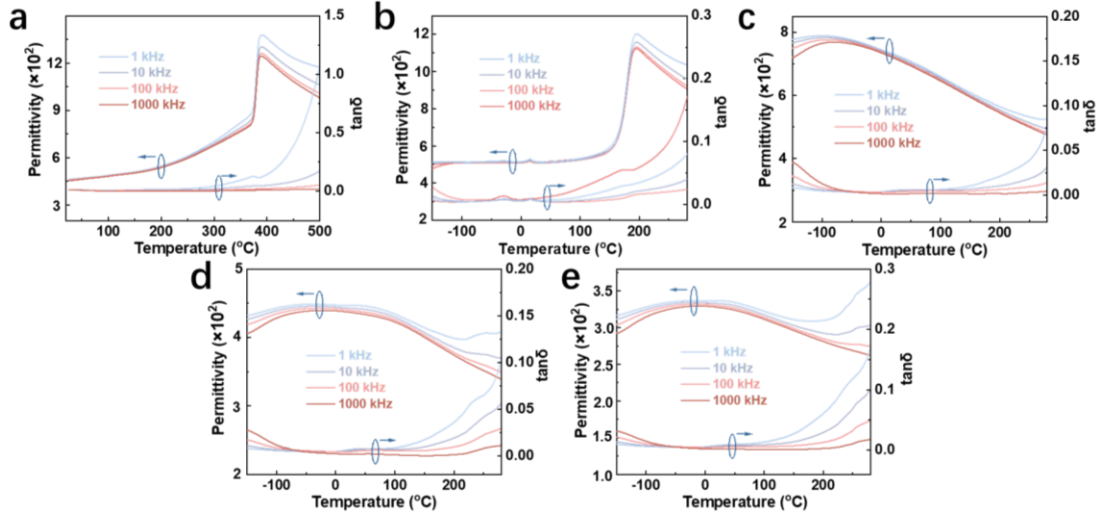
Supplementary Fig. 18 Evolution of average grain size of the $(1-x)\text{NN}-x\text{BNH}$ ceramics.



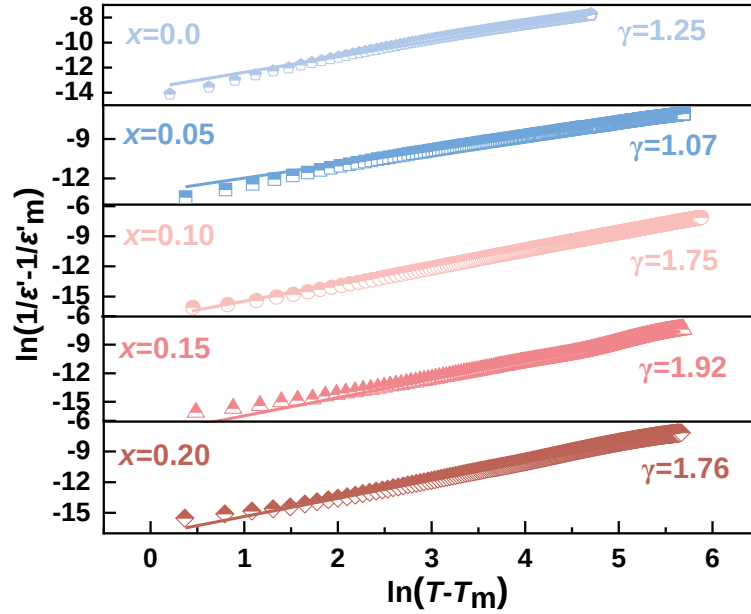
Supplementary Fig. 19 Z* plots at various temperatures for **a** $x=0$, **b** $x=0.05$, **c** $x=0.15$.
d Z* plots as a function of frequency measured at 500 °C for (1-x)NN-xBNH ceramics.



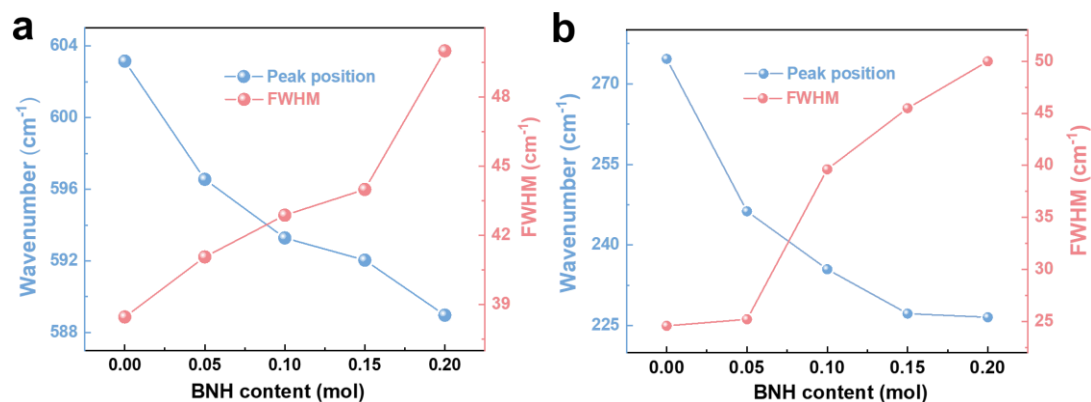
Supplementary Fig. 20 Conductivity as a function of frequency measured at 500 °C for (1-x)NN-xBNH ceramics.



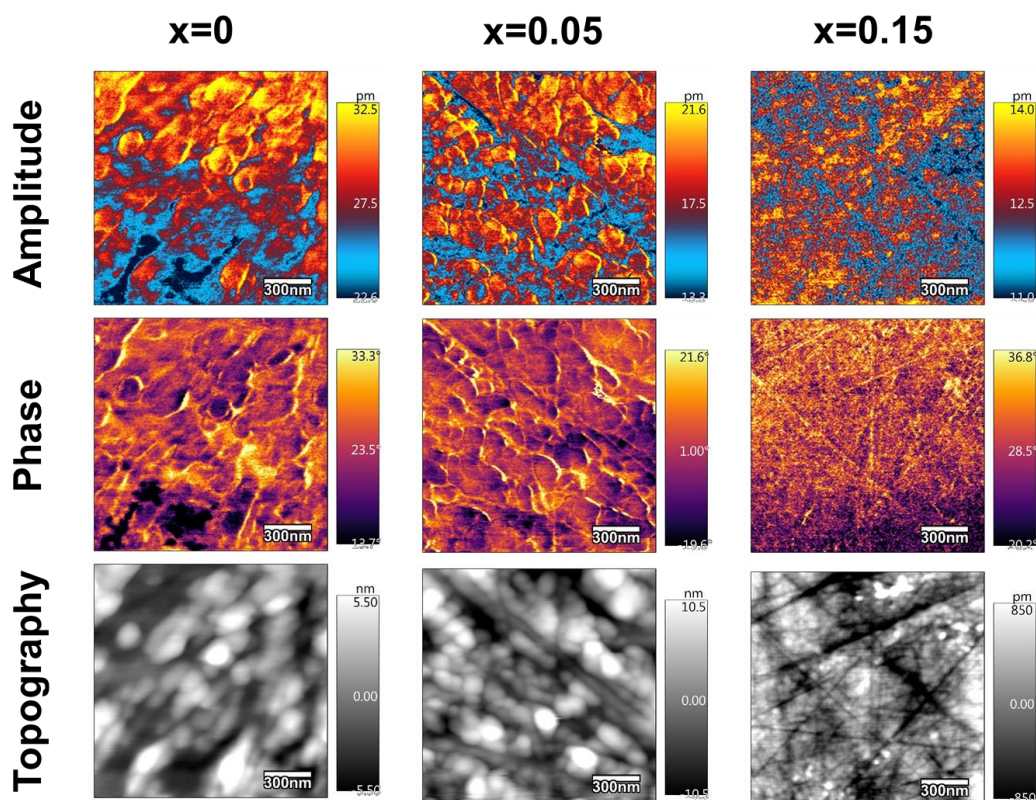
Supplementary Fig. 21 Dielectric constant and dielectric loss as a function of temperature at various frequencies for **a** $x=0$, **b** $x=0.05$, **c** $x=0.10$, **d** $x=0.15$, **e** $x=0.20$.



Supplementary Fig. 22 $\ln(1/\epsilon' - 1/\epsilon'_m)$ versus $\ln(T - T_m)$ for (1-x)NN-xBNH ceramics at 1MHz. The relaxor diffuseness factor γ can be calculated from the modified Curie-Weiss law, $\frac{1}{\epsilon'} - \frac{1}{\epsilon'_m} = \frac{(T - T_m)^\gamma}{C}$, where ϵ' is the permittivity at the temperature T , T_m is the temperature at which ϵ' reaches the maximum value (ϵ'_m), and C is a constant. The γ value is used to reflect the relaxor feature, which varies from 1 (corresponding to normal ferroelectrics) to 2 (corresponding to ideal relaxors).



Supplementary Fig. 23 The variation in wavenumber and FWHM of **a** v_1 and **b** v_5 Raman vibration modes.



Supplementary Fig. 24 PFM amplitude images, phase images and topography images of $x=0$, $x=0.05$ and $x=0.15$ ceramics.

Supplementary Table 1. Comparison of quadrupolar coupling constants C_Q , isotropic chemical shifts δ_{iso} , asymmetry η and quadrupolar product P_Q for $x=0$ and $x=0.15$ materials. The data are derived from line shape simulations shown in Fig. S13, which are based on negatively correlated Gaussian distributions for both NMR parameters.

Sample	C_Q (kHz)	δ_{iso} (ppm)	η	P_Q (kHz)
$x=0$	1043	-4.50	0.198	1207
$x=0.15$	813	-6.42	0.844	1722