

Supplementary Information for

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

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Supplementary Note 1: Atomic configuration entropy calculation

Configurational entropy, a crucial thermodynamic quantity that quantifies the degree of disorder in the arrangement of components within a system, which can be calculated using the following equation:

$$S_{config} = -R \left[\left(\sum_{i=1}^N x_i \ln x_i \right)_{cation-site} + \left(\sum_{j=1}^M x_j \ln x_j \right)_{anion-site} \right] \quad (1)$$

Here, R represents the ideal gas constant, while x_i and x_j denote the mole fraction of the i -th cation and j -th anion components, respectively. To delineate the various categories of high-entropy ceramics (HECs), the factor R from the ideal configurational entropy equation is utilized. HECs are identified by a configurational entropy $S_{config} > 1.5R$. Medium-entropy ceramics (MECs), have S_{config} ranging $1R$ to $1.5R$, while low-entropy ceramics are characterized by $S_{config} < 1R^{1-3}$.

Supplementary Note 2: Design considerations for A-site/B-site doping and multi-element selection rules

Firstly, the selection of Sr^{2+} (1.44 Å) as the A-site cation introduces further local disorder due to its size mismatch with Bi^{3+} (1.35 Å) and Na^+ (1.39 Å), thereby amplifying the random electric field and aiding in the destabilization of macroscopic ferroelectric domains^{4,5}. In addition, Sr doping is 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^{6,7}.

Meanwhile, based on charge neutrality and valence compensation considerations, a combination of Sc^{3+} and Ta^{5+} was chosen to substitute for Ti^{4+} 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 Sc^{3+} (0.75 Å) and Ta^{5+} (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^{4,8}.

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 failure⁹.

Supplementary Note 3: The fabrication of 1.88R-BC and 1.88R-RRP

Bulk ceramics preparation

The entropy-modulated dielectric ceramics with the compositional formula $(1-x)\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3$ - $x\text{Sr}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ (abbreviated as BNKT- x , $x = 0, 0.05, 0.10, 0.15, 0.20$ and 0.25) were synthesized using a conventional solid-state reaction technique. The specific configuration entropy values (S_{config}) for each component are

summarized in Table S1. High-purity oxides and carbonates, including Bi_2O_3 ($\geq 99.9\%$, Aladdin), Na_2CO_3 ($\geq 99.8\%$, Aladdin), K_2CO_3 ($\geq 99.5\%$, Aladdin), TiO_2 ($\geq 99.9\%$, Aladdin), SrCO_3 ($\geq 99.5\%$, Aladdin), Sc_2O_3 ($\geq 99.9\%$, Aladdin) and Ta_2O_5 ($\geq 99.99\%$, Aladdin) were used as the raw materials. The pre-dried powders were weighed according to their stoichiometric ratios, with an additional 2 wt.% of Bi_2O_3 , Na_2CO_3 , and K_2CO_3 added to compensate for potential volatilization during high-temperature sintering. The weighed powders were mixed and ball-milled in ethanol for 24 hours at 300 rpm using Y_2O_3 -stabilized zirconia milling media. After drying, the mixtures were calcined at 800-850 °C for 4 hours. The calcined powders were then subjected to a second round of ball milling, followed by drying and sieving. The processed powders were uniaxially pressed into 12 mm diameter green ceramic sheets at 10 MPa and further compacted through cold isostatic pressing at 300 MPa for 5 minutes. To prevent the evaporation of volatile elements such as Bi, Na, and K during sintering, the samples were embedded in powders of the same composition. Finally, sintering was conducted at 1160-1200 °C for 4 hours with a heating rate of 2 °C min⁻¹ in closed alumina crucibles. For electrical measurements, silver paste was applied to both surfaces of the sintered samples and fired at 600 °C for 30 minutes to form electrodes. Notably, 1.88R-BC sintered at 1190 °C exhibited the highest relative density (up to 98.3%), and achieved the maximum E_b under this optimized condition (see Supplementary Fig. 28.) 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.

Repeated rolling processing

The BNKT-0.20 green ceramic thick films with a configurational entropy of $S_{\text{config}} = 1.88R$ were fabricated by a repeated rolling processing (RRP) technique, employing pre-sintered powders as the raw materials. After drying and sieving, the matrix powders were blended with the polyvinyl alcohol (PVA) at a 3:1 mass ratio through high-energy ball milling at 1500 rpm for 2 hours. The resulting ceramic tapes produced were then punched into 12 mm diameter disks and calcined at 650 °C for 4 hours to eliminate the organic binder. Subsequently, the green disks were embedded in the pre-sintered powders of the identical composition and sintered at 1080-1150 °C for 3 hours using a double crucible method with a heating rate of 4 °C min⁻¹.

Supplementary Note 4: Phase-field simulations

Phase-field simulations of Bi_{0.5}Na_{0.5}TiO₃-based solid solutions are conducted to investigate the composition-dependent evolution of domain structures, material properties, and underlying mechanisms. The temporal evolution of spatially inhomogeneous polarization behavior within the ferroelectric layer, based on the principle of energy minimization, is described by the time-dependent Ginzburg-Landau (TDGL) equation¹⁰⁻¹²:

$$\frac{\partial P_i(r,t)}{\partial t} = -L \frac{\delta F}{\delta P_i(r,t)}, (i = 1,2,3) \quad (2)$$

where L is the kinetic coefficient governing domain switching, r and t are the spatial coordinate and time, and F represents the total free energy of the system, defined as:

$$F = \int (f_{\text{bulk}} + f_{\text{grad}} + f_{\text{elas}} + f_{\text{elec}}) dV \quad (3)$$

where f_{bulk} , f_{grad} , f_{elas} and f_{elec} representing the contributions from bulk free energy, gradient energy, elastic strain energy, and electric energy, respectively. The bulk free energy is expressed as:

$$\begin{aligned} f_{\text{bulk}} = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2 P_2^2 + P_2^2 P_3^2 + P_1^2 P_3^2) \\ & + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) + \alpha_{112}[(P_1^4(P_2^2 + P_3^2) + (P_2^4(P_1^2 + P_3^2) + (P_3^4(P_1^2 + \\ & P_2^2)] + \alpha_{123}P_1^2 P_2^2 P_3^2 \end{aligned} \quad (4)$$

where P_1 , P_2 , and P_3 are polarization components, and α_1 , α_{11} , α_{12} , α_{111} , α_{112} , and α_{123} represent the Landau coefficients¹³. The Landau parameters are specified as follows: $\alpha_1 = 4.124 \times 10^5 (T - T_0)$, $\alpha_{11} = -5 \times 10^8 (c - c_0)$, $\alpha_{12} = 8.0 \times 10^8 (c - c_0) + 2\alpha_{11}$, $\alpha_{111} = 1.294 \times 10^9 (c - c_0)$, $\alpha_{112} = 1.5 \times 10^9 (c - c_0) + 3\alpha_{111}$, $\alpha_{123} = 7.5 \times 10^8 (c - c_0) + 6\alpha_{123}$.

Gradient energy, which reflects domain-wall energy stemming from inhomogeneous polarization distribution, is described by:

$$f_{\text{grad}} = \frac{1}{2} G_{ijkl} P_{i,j} P_{k,l} \quad (5)$$

where $P_{i,j} = \partial P_i / \partial x_j$ and G_{ijkl} is the gradient energy coefficient.

The elastic strain energy is formulated as:

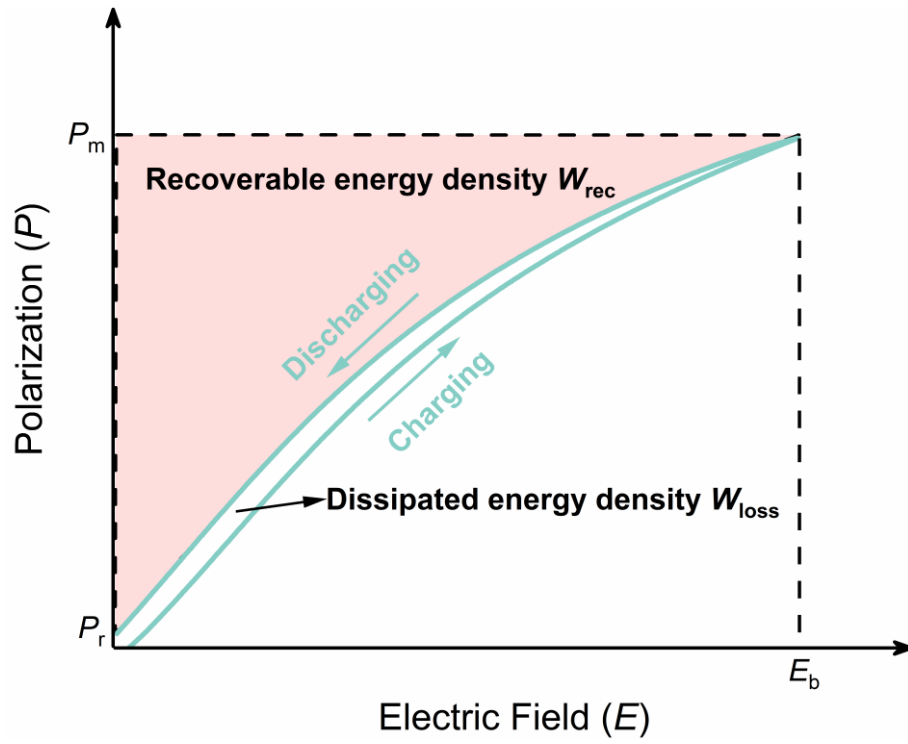
$$f_{\text{elas}} = \frac{1}{2} C_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0) (\varepsilon_{kl} - \varepsilon_{kl}^0) \quad (6)$$

with C_{ijkl} as the elastic stiffness tensor, ε_{ij} as the total local strain, and ε_{ij}^0 as the eigenstrain, respectively. which incorporates local strain fluctuations $\varepsilon^{\text{rand}}$ modeled by Gaussian distribution. The electric energy density is defined as:

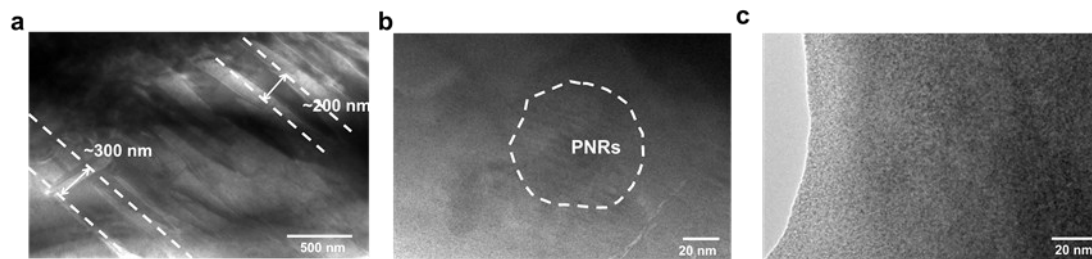
$$f_{\text{elec}} = -P_i(r) E_i^{\text{ex}}(r) - \frac{1}{2} P_i(r) E_i^{\text{in}}(r) \quad (7)$$

where E^{ex} is the external electric field, and E^{in} encompasses the internal electric field,

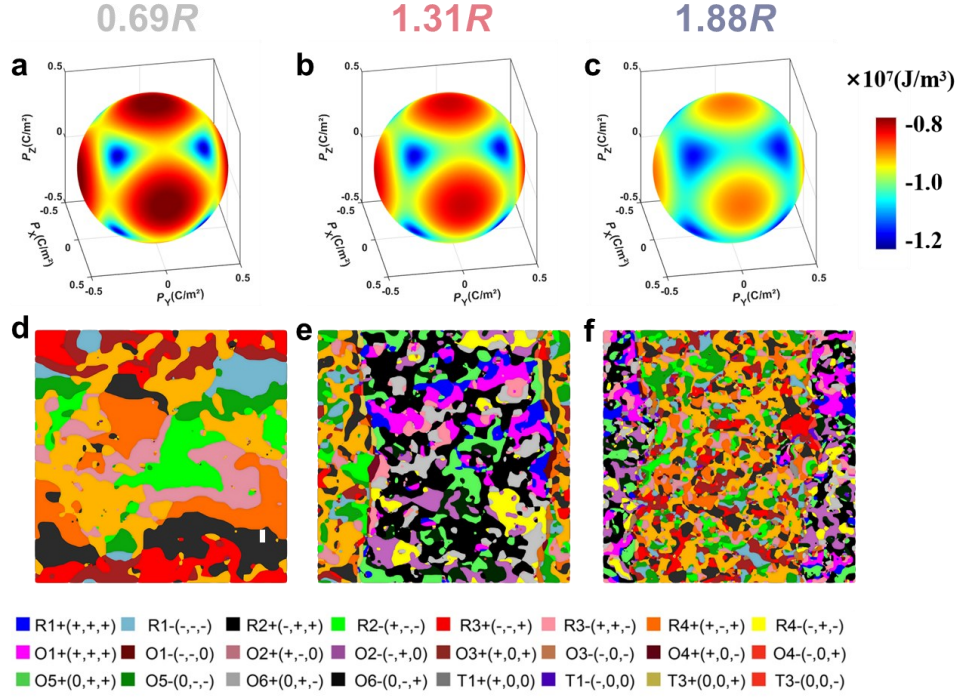
including dipole-dipole interactions and local electric fields arising from random point defects. In this model, 5% - 20% of randomly distributed points are categorized as defect dipoles.



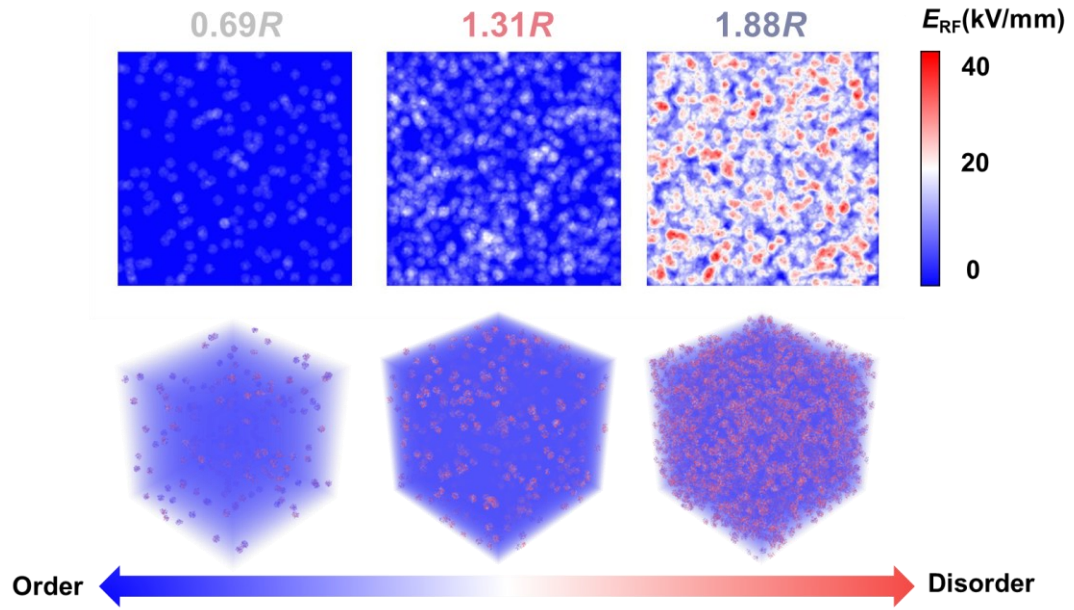
Supplementary Fig. 1 Graphical representation of energy storage performance (ESP) calculation for dielectric materials. The ESP was quantified by calculating the integral of the polarization-electric field (P - E) hysteresis loop. In dielectric capacitors, the charging process induces polarization in the dielectric material, enabling the storage of electrostatic energy. Conversely, during discharging, this polarization is released, allowing for the retrieval of stored energy, referred to as recoverable energy density (W_{rec}), represented by the pale pink area. The recoverable energy density is expressed as the integral $W_{rec} = \int_{P_r}^{P_m} E dP$, where P_m represents the maximum polarization, and P_r donates the remnant polarization. The efficiency η is defined as $\eta = W_{rec} / (W_{rec} + W_{loss})$, where W_{loss} is the energy lost during discharging, corresponding to the area enclosed by the P - E loop. The total energy storage density W_{tot} is thus calculated by $W_{tot} = W_{rec} + W_{loss}$. The breakdown strength E_b refers to the maximum electric field that a dielectric material can withstand before electrical conduction.



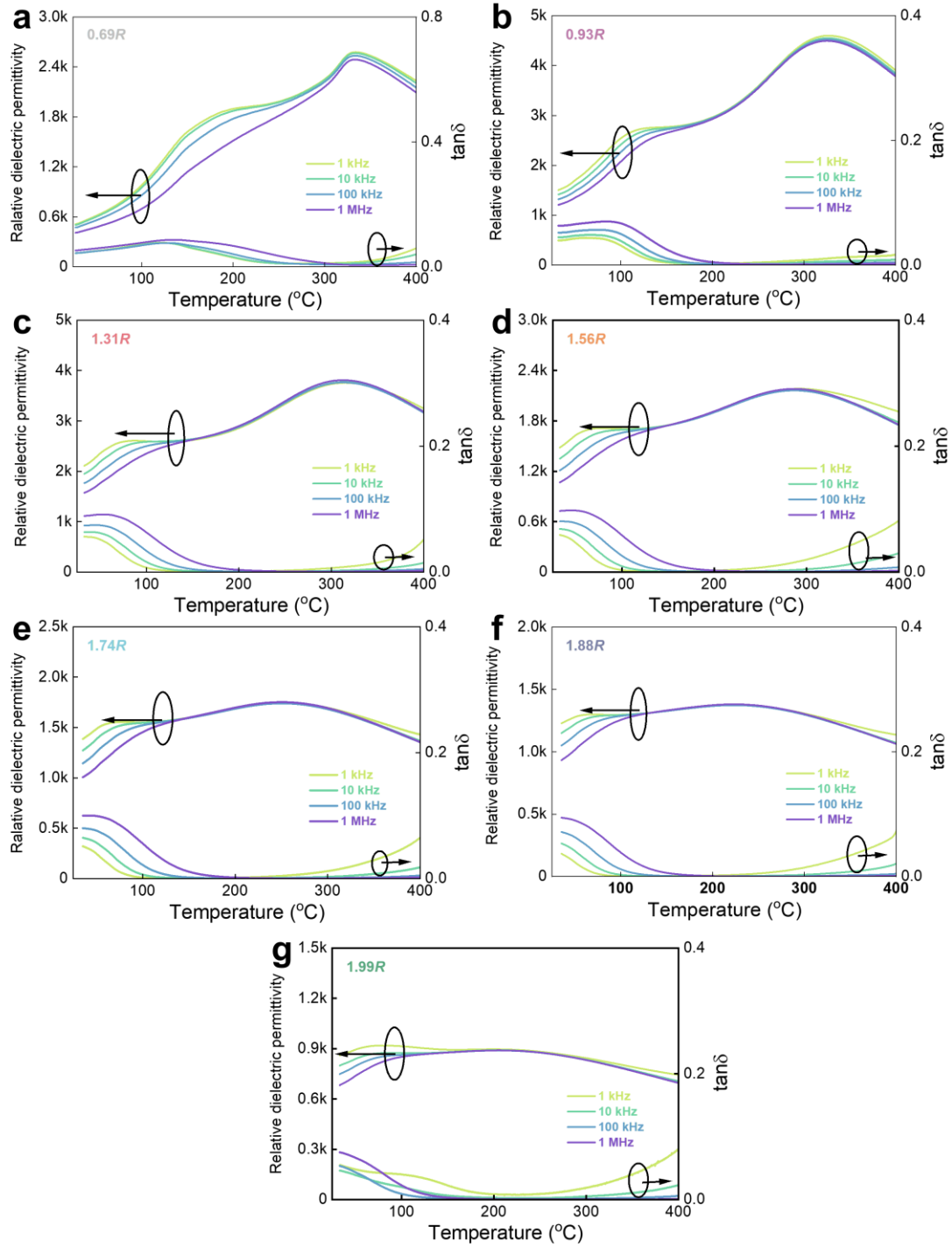
Supplementary Fig. 2 HR-TEM micrographs of a BNT, b, 1.88R-BC, and c, 1.88R-MLCCs. We have conducted HR-TEM analysis on the BNT (0.69R), 1.88R-BC, and 1.88R-MLCCs samples. The results reveal that in BNT ceramics, ordered stripe domains with widths of 200 nm and 300 nm are observed within the grains, 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. 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.



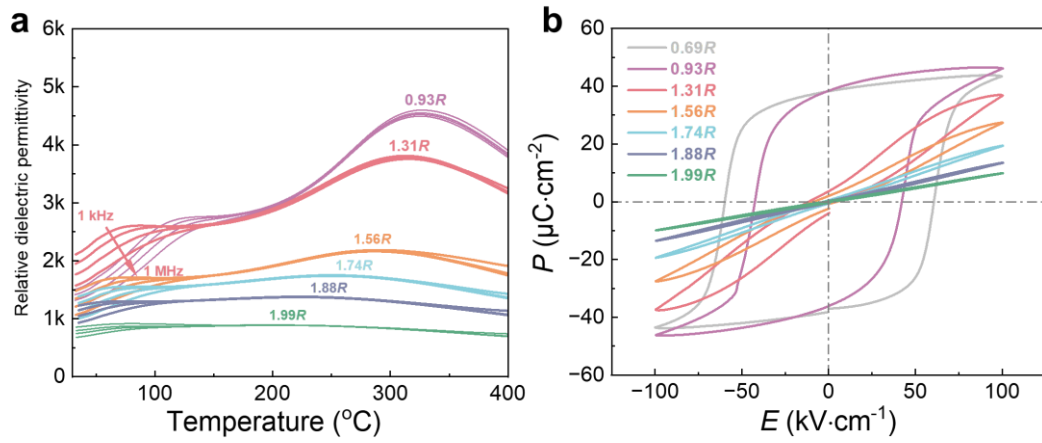
Supplementary Fig. 3 Evolution of polar structures simulated by the phase-field model. (a to c) Landau free-energy profiles; (d to f) simulated domain structures for (a, d) 0.69R, (b, e) 1.31R, and (c, f) 1.88R. Among the phases, the *R* phase represents the lowest-energy state, while the *T* phase corresponds 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.



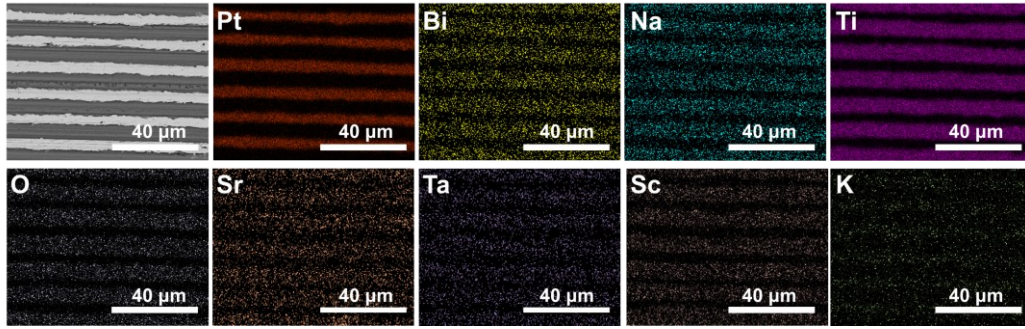
Supplementary Fig. 4 The distribution of simulated random field in the X-Y plane and three-dimensional space for $0.69R$, $1.31R$, and $1.88R$. With increasing configurational entropy of the system, the intensity of the random field strengthens, and the degree of disorder intensifies.



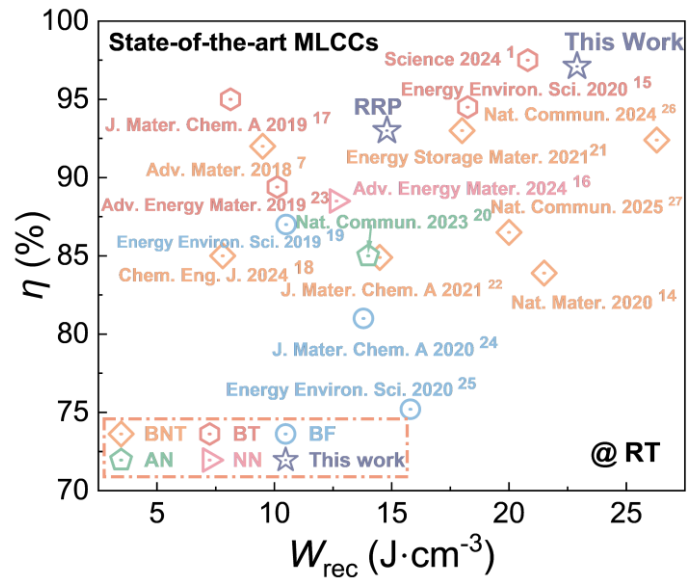
Supplementary Fig. 5 Temperature-dependent dielectric permittivity and $\tan\delta$ with different frequencies for the a BNT (0.69R) and (1-x)BNKT-xSST ceramics: b $x = 0$ (0.93R), c $x = 0.05$ (1.31R), d $x = 0.10$ (1.56R), e $x = 0.15$ (1.74R), f $x = 0.20$ (1.88R), g $x = 0.25$ (1.99R).



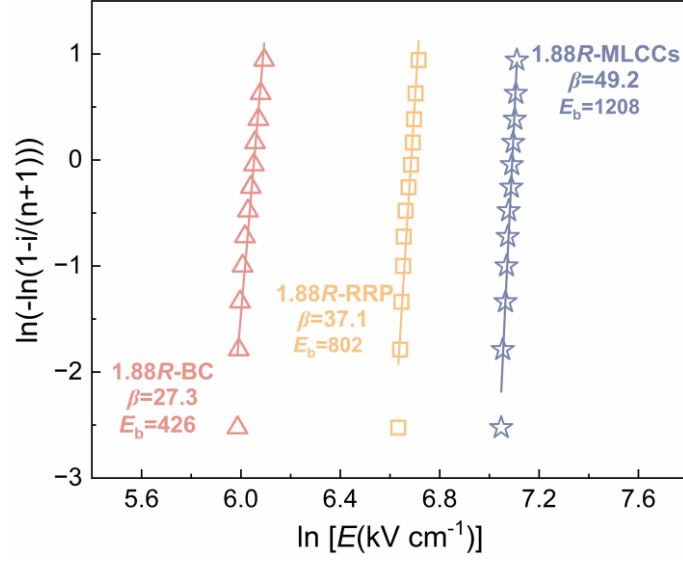
Supplementary Fig. 6 Dielectric and ferroelectric properties of the BNT-based ceramics. a, Temperature and frequency-dependent dielectric spectra. **b,** Unipolar P - E hysteresis loops at 100 kV cm^{-1} .



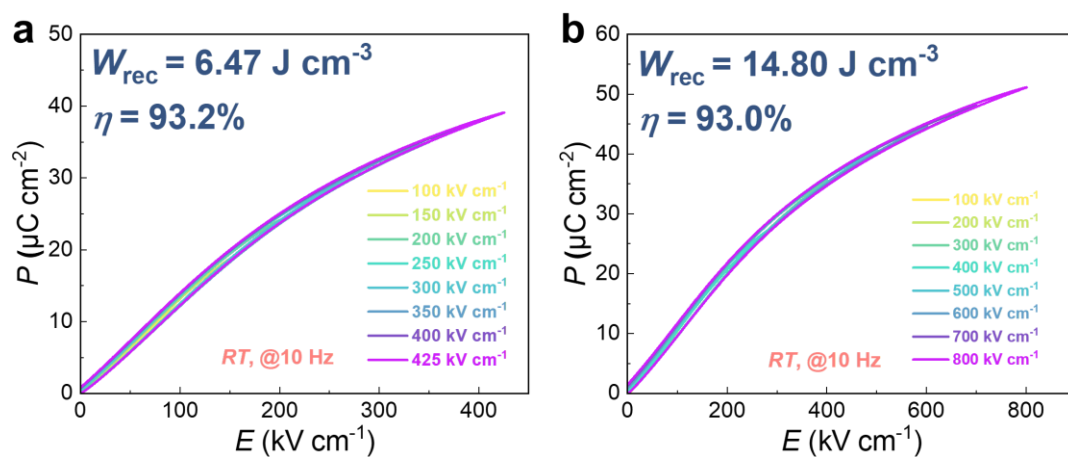
Supplementary Fig. 7 The cross-sectional SEM micrograph and Energy-dispersive X-ray spectrometry (EDS) element-mapping images of the BNT-based MLCC with $S_{\text{config}} = 1.88R$. The finely-sintered multilayer capacitors display a dense internal microstructure with distinct electrode and dielectric layer interfaces, and a homogenous elemental distribution with no evidence of segregation.



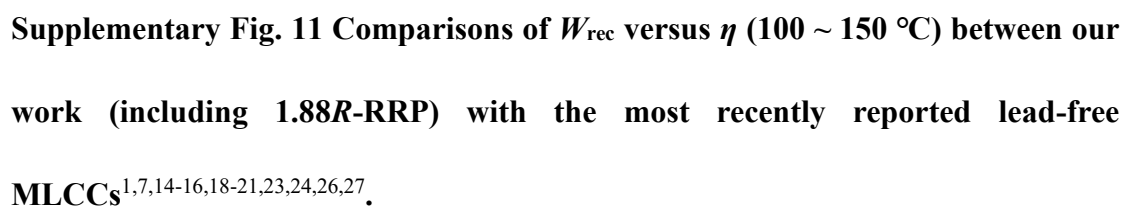
Supplementary Fig. 8 Comparisons of W_{rec} and η between our work (including 1.88R-RRP) with the state-of-the-art lead-free MLCCs at room temperature^{1,7,14-27}. Even with an energy storage characteristic of 1.88R-RRP, it demonstrates excellent performance compared to several recently reported advanced MLCCs.

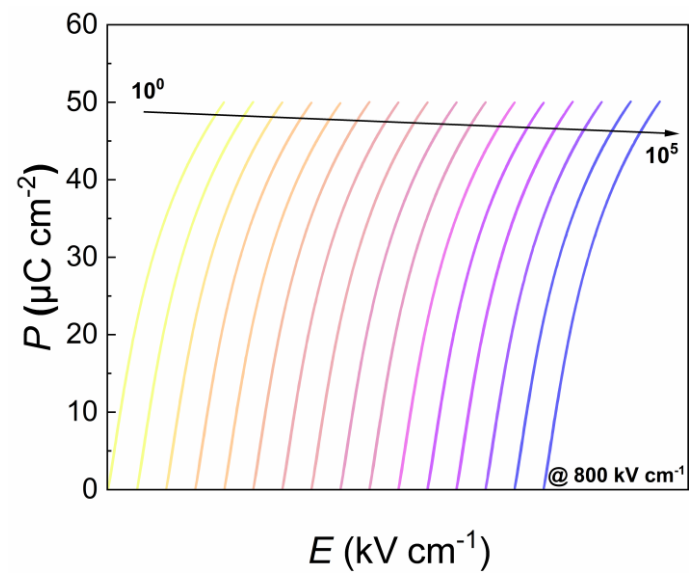


Supplementary Fig. 9 Weibull distribution fitting lines of breakdown strength E_b for 1.88R-BC, 1.88R-RRP, and 1.88R-MLCCs, separately. The Weibull modulus β values increases from 27.3 for 1.88R-BC to 37.1 for 1.88R-RRP, reaching 49.2 for 1.88R-MLCCs, indicating a more homogenous data distribution and enhanced reliability of the E_b values.

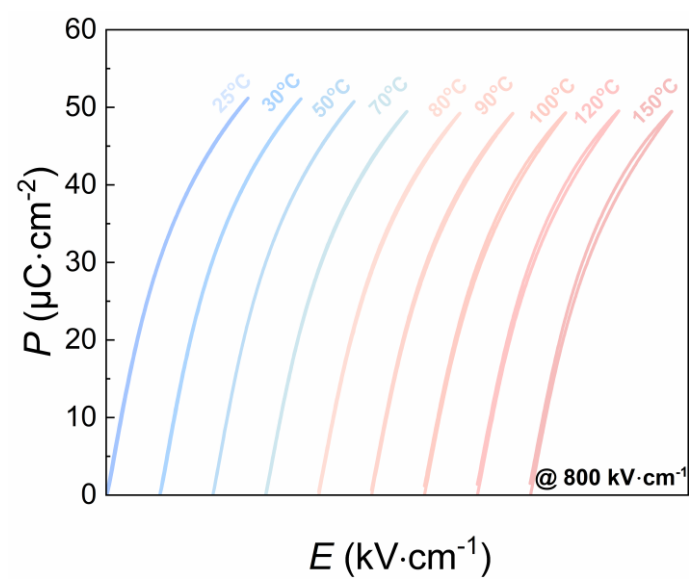


Supplementary Fig. 10 Room-temperature P - E loops as a function of electric field up to E_b at 10 Hz. **a**, 1.88R-BC, **b**, 1.88R-RRP.

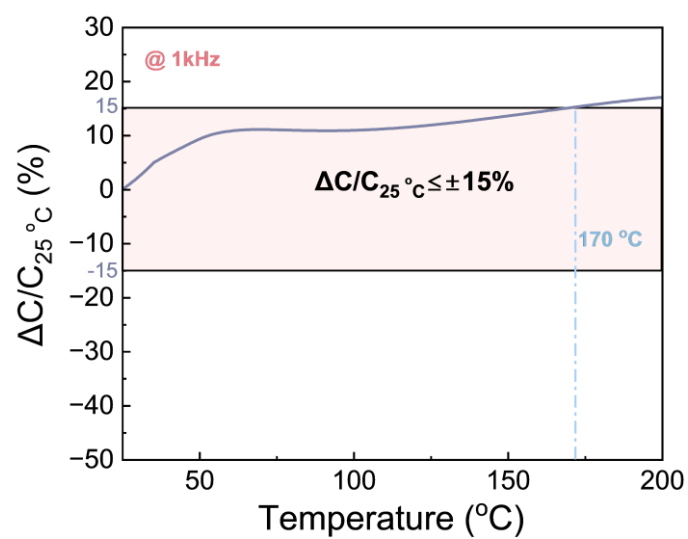




Supplementary Fig. 12 Unipolar P - E hysteresis loops of 1.88R-MLCCs as a function of the cycling numbers (1- 10^5) under 800 kV cm⁻¹.

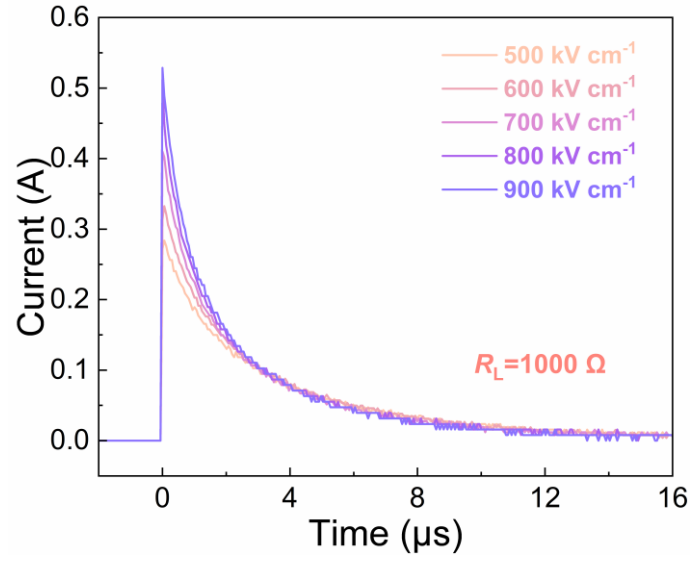


Supplementary Fig. 13 Temperature-dependent unipolar P - E hysteresis loops of 1.88R-MLCCs at $800 \text{ kV} \cdot \text{cm}^{-1}$.

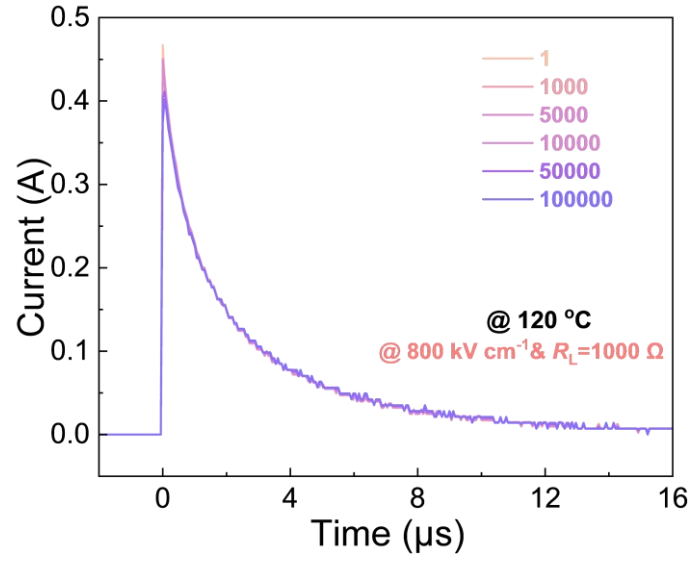


Supplementary Fig. 14 Variation of temperature-dependent capacitance deviation

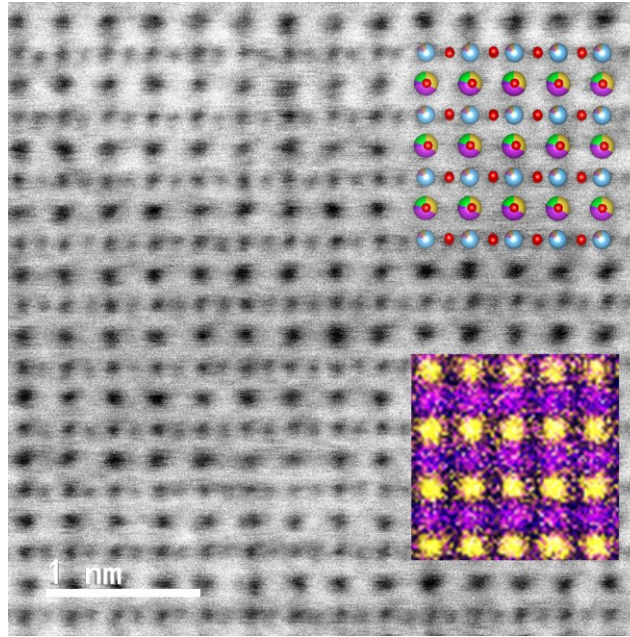
($\Delta C/C_{25\text{ }^{\circ}\text{C}}$) at 1 kHz.



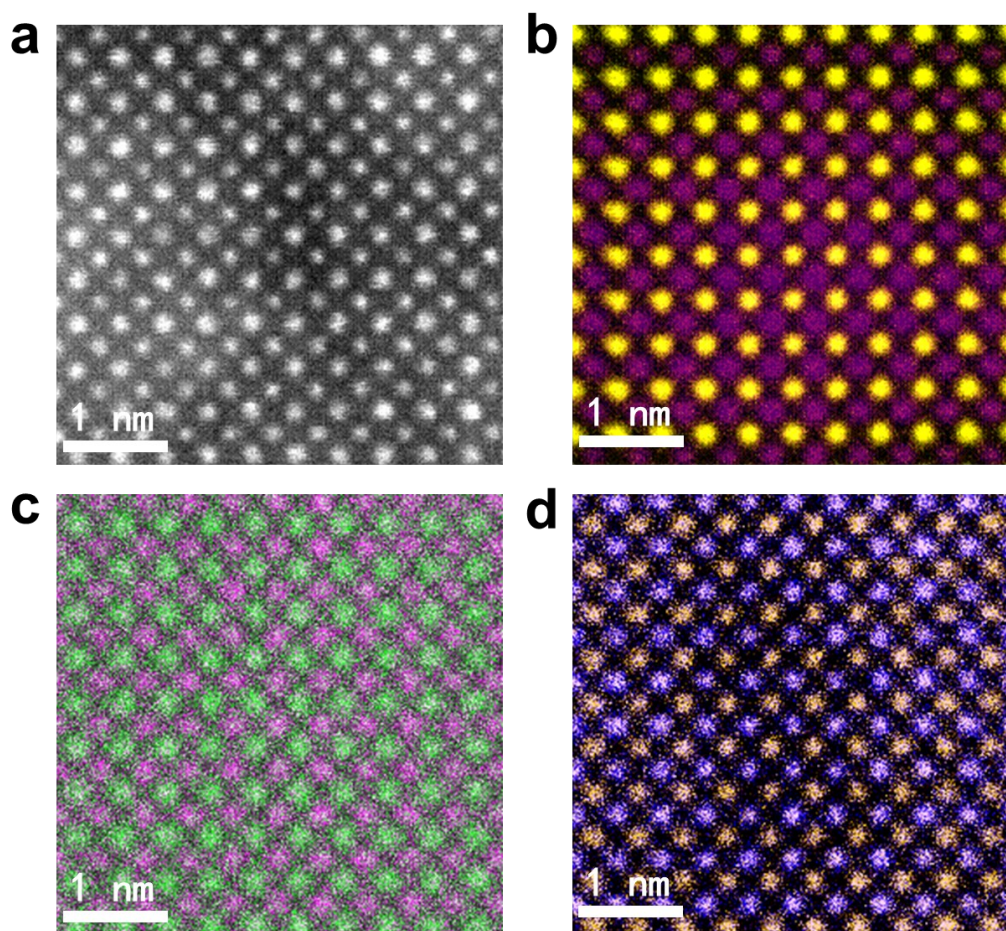
Supplementary Fig. 15 Overdamped discharging current as a function of time at various electric fields for 1.88R-MLCCs.



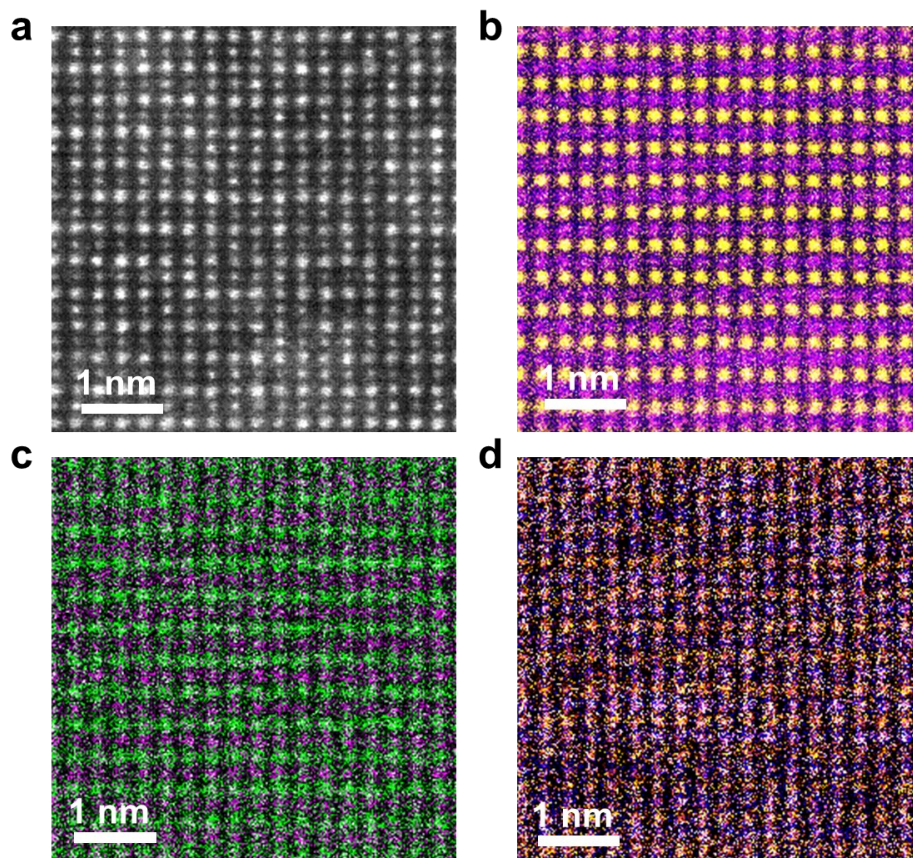
Supplementary Fig. 16 Overdamped discharging current as a function of time for 1.88R-MLCCs cycling stability (1-10⁵) under 800 kV cm⁻¹ at 120 °C.



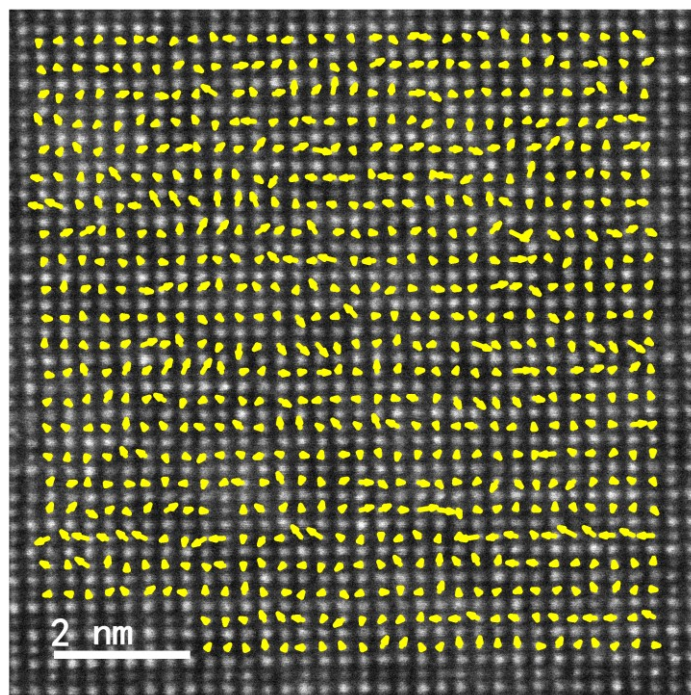
Supplementary Fig. 17 AC-BF-STEM image along the [110] direction at high magnification. Inset: Crystal structure simulation (top-right) and atomic EDS mapping showing the element distributions of Bi and Ti (purple and yellow spheres, respectively).



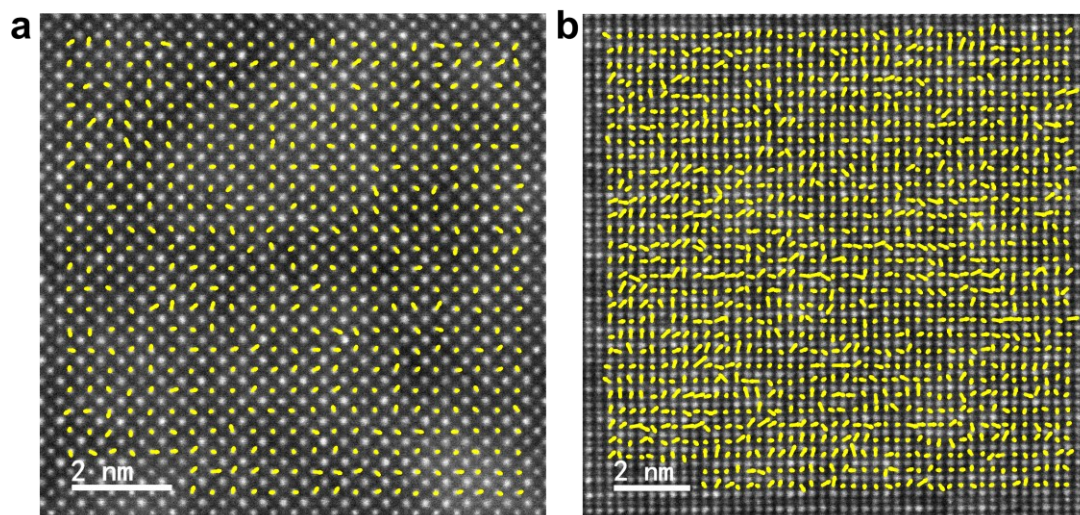
Supplementary Fig. 18 AC-HAADF-STEM image (a) and atomic EDS mapping of element distributions (b to d) along the [100] direction of the BNT-based MLCC with $S_{\text{config}} = 1.88R$. **b**, Bi and Ti (purple and yellow spheres, respectively), **c**, Na and Sc (green and pink spheres, respectively), **d**, Sr and Ta (pale amber and lavender spheres, respectively).



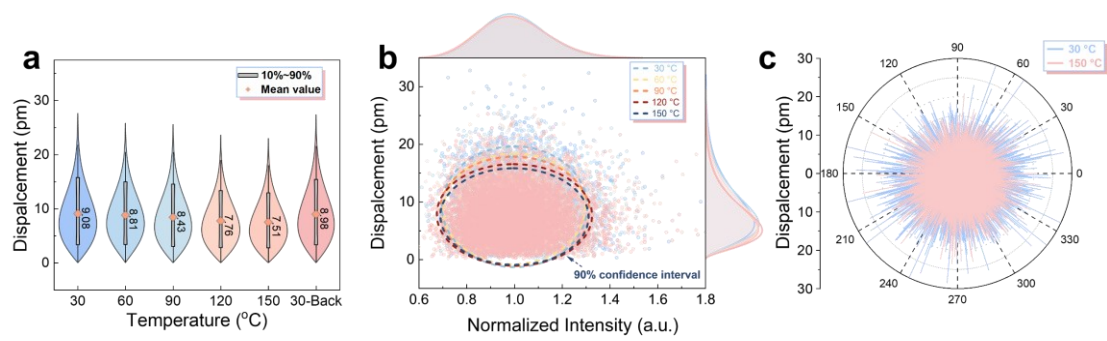
Supplementary Fig. 19 AC-HAADF-STEM image (a) and atomic EDS mapping of element distributions (b to d) along the [110] direction of the BNT-based MLCC with $S_{\text{config}} = 1.88R$. **b**, Bi and Ti (purple and yellow spheres, respectively), **c**, Na and Sc (green and pink spheres, respectively), **d**, Sr and Ta (pale amber and lavender spheres, respectively).



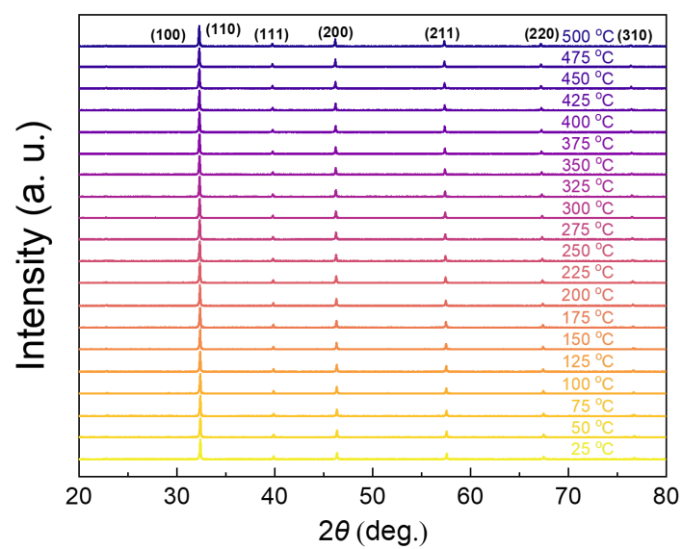
Supplementary Fig. 20 AC-HAADF-STEM polarization vector image along the [110] direction of the BNT-based MLCC with $S_{\text{config}} = 1.88R$ at 30 °C.



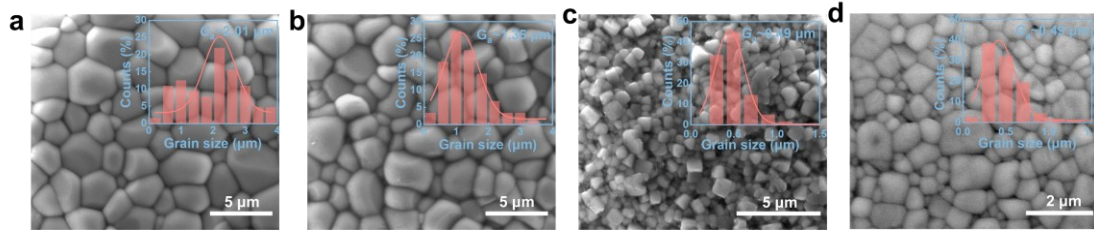
Supplementary Fig. 21 AC-HAADF-STEM polarization vector image along the 100 and 110 axes of the BNT-based MLCC with $S_{\text{config}} = 1.88R$ at 150 °C. **a, 100 axes. **b**, 110 axes.**



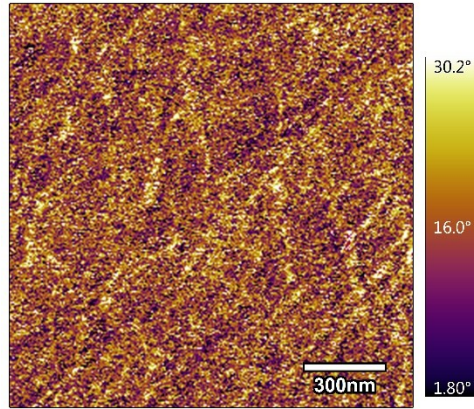
Supplementary Fig. 22 Local structural characterizations of 1.88R-MLCCs. a, b, Statistical analysis of cation displacements (**a**), normalized atomic intensities (**b**) as a function of temperatures, **c**, polar mapping of cations displacement distributions by magnitudes and directions at various temperatures along the [110] direction.



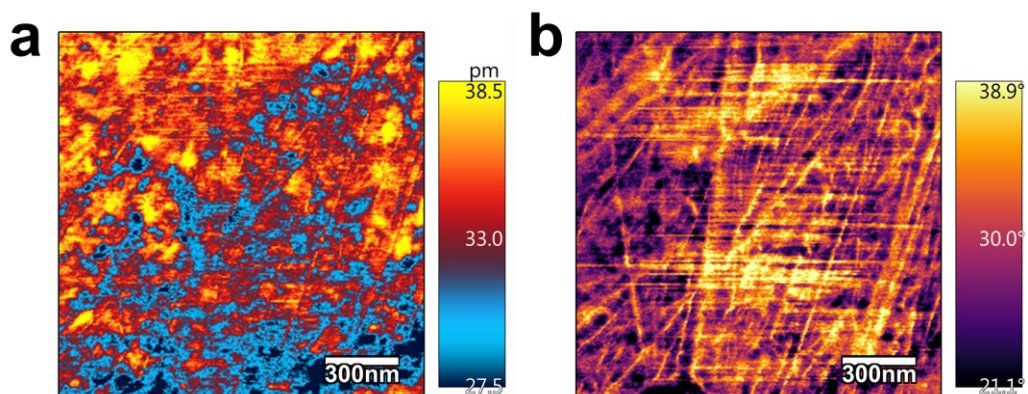
Supplementary Fig. 23 Temperature-dependent PXRD patterns of the 1.88R from 25 to 500 °C.



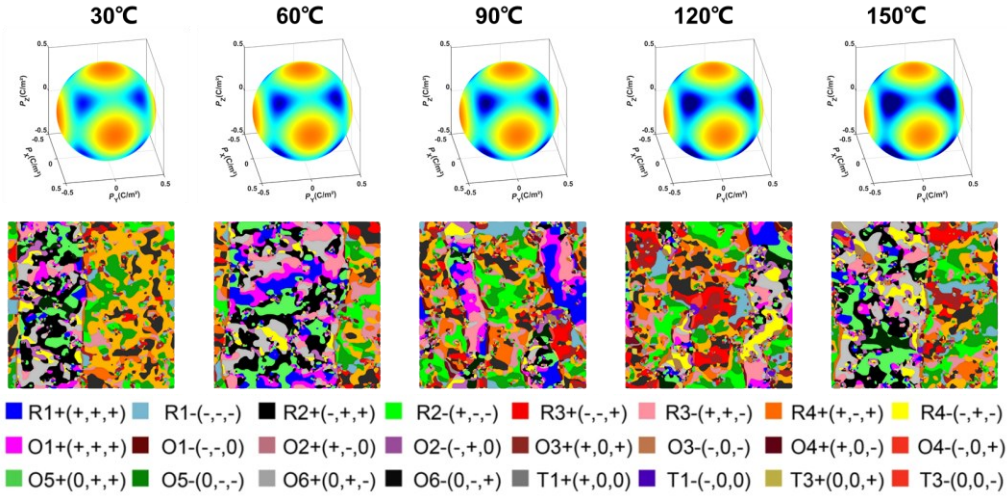
Supplementary Fig. 24 SEM morphology and grain size distribution. Natural surfaces SEM morphology of **a**, 1.88R-BC, **b**, 1.88R-RRP, and **c**, 1.88R-MLCCs, along with **d**, thermal etching surface morphology of 1.88R-MLCCs. We performed polishing and thermal etching on the natural surfaces of the samples. The grain size distributions obtained from these treated surfaces were statistically analyzed using Nano Measurer software, and the results are consistent with those based on surface morphology.



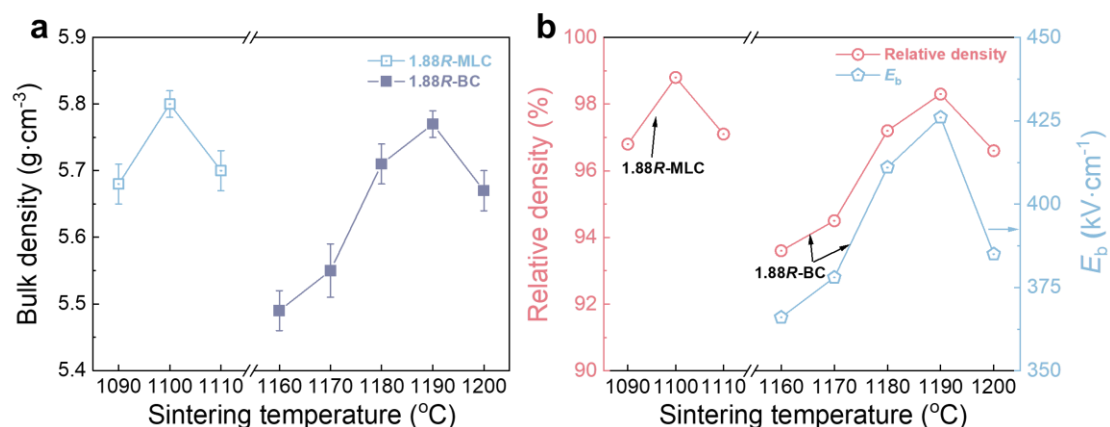
**Supplementary Fig. 25 Out-of-plane PFM phase images the BNT-based MLCC
with $S_{\text{config}} = 1.88R$.**



Supplementary Fig. 26 Out-of-plane PFM (a) amplitude and (b) phase images of 1.88R-RRP.



Supplementary Fig. 27 Temperature-dependent Landau free-energy profiles and simulated domain structures. In the simulation, the Landau energy parameter α_1 incorporates a temperature-dependent term, which describes the trend of increasing Landau energy with rising temperature. This trend aligns with the experimental observation that the saturation polarization slightly decreases as the temperature increases.



Supplementary Fig. 28 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. The error bars represent the positive and negative deviations from the average value, corresponding to the differences between the average and the maximum/minimum values measured across multiple independent samples. The average values were obtained from multiple samples prepared under identical sintering conditions. **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. Sintering of 1.88R-BC (with a theoretical density of 5.87 g cm^{-3}) within the temperature range of 1160-1200 $^{\circ}\text{C}$ consistently results in effective densification. Samples sintered at 1190 $^{\circ}\text{C}$ exhibit the highest relative density of up to 98.3% and achieve the maximum E_b under this optimized condition. For comparison, the relative densities of 1.88R-MLC sintered at various temperatures are also marked in the same chart, showing that its relative density peaked at 1100 $^{\circ}\text{C}$.

Supplementary Table 1 The configurational entropy of the BNT-based ceramics.

Compositions	S_{config}
BNT	$0.69R$
BNKT	$0.93R$
BNKT-0.5SST	$1.31R$
BNKT-1.0SST	$1.56R$
BNKT-1.5SST	$1.74R$
BNKT-2.0SST	$1.88R$
BNKT-2.5SST	$1.99R$

Supplementary Table 2 Comparisons of comprehensive properties (W_f , W_{rec} , η , E_b , P_{max} , ΔP , $W_{\text{rec}} \sim 150$ °C, and $\eta \sim 150$ °C) for 1.8R-BC, 1.88R-RRP, and 1.88R-MLCCs.

	1.8R-BC	1.88R-RRP	1.88R-MLCCs
W_f	96	211	800
W_{rec} (J cm ⁻³)	6.47	14.80	22.92
η (%)	93.2	93.0	97.1
P_{max} (μC·cm ⁻²)	39.0	51.1	58.5
ΔP (μC·cm ⁻²)	38.1	49.5	58.0
W_{rec} (J cm ⁻³) ~ 150 °C	3.55	9.26	13.77
η (%) ~150 °C	89.2	91.6	92.3

Supplementary Table 3 Renormalized coefficients derived from the fitting of X-ray total scattering $G(r)$ data of 1.88R-MLCCs.

Parameters		T phase	R phase
		$P4bm$	$R3c$
Space Group		(No. 100)	(No. 161)
Scale Factor		0.818(5)	0.182(5)
$a / \text{\AA}$		5.5712(5)	5.6294(3)
$c / \text{\AA}$		3.3981(6)	13.9579(7)
R_{wp}		11.94 %	
A site	x	0	0
	y	0.5	0
	z	0.5422(18)	0.5112(48)
	$B_{\text{iso}}/10^2 \text{\AA}^2$	6.90 (60)	8.73(42)
B site	x	0	0
	y	0	0
	z	0.0061(15)	0.2123(34)
	$B_{\text{iso}}/10^2 \text{\AA}^2$	2.08 (27)	2.58(18)
O1	x	0	0.1417(22)
	y	0	0.3372(31)
	z	0.4779 (24)	0.3621(32)
	$B_{\text{iso}}/10^2 \text{\AA}^2$	1.38 (46)	1.37 (52)
O2	x	0.2637(32)	0.8084(48)
	y	0.2637(32)	0.6705(34)
	z	0.9083(41)	0.6954(36)
	$B_{\text{iso}}/10^2 \text{\AA}^2$	3.61 (15)	1.37 (52)
O3	x		0.4750(29)
	y		0.0039(31)
	z		0.0288(28)
	$B_{\text{iso}}/10^2 \text{\AA}^2$		1.37 (52)

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