Supporting Information

Improved Capacitive Energy Storage in K_{0.5}Na_{0.5}NbO₃-based High-entropy Ceramics with Order-disorder Polarization Configuration

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Experimental

The $K_{(1-x)/2}Na_{(3-2x)/6}Sr_{x/3}Bi_{x/2}Ni_{x/6}Al_{x/6}Hf_{x/2}Ta_{x/6}Nb_{(1-x)}O_3$ (x=0, 0.1, 0.15, 0.2, 0.25) ceramics were synthesized by a traditional solid-state technique. All raw materials are purchased from Sinopharm Chemical Reagent Co., Ltd. The powders of K₂CO₃(99.5%), Na₂CO₃(99.8%), Nb₂O₅(99.5%), Bi₂O₃(99.9%), NiO(99.9%), SrCO₃(99.5%), Al₂O₃(99.99%), HfO₂(99.9%), Ta₂O₅(99.99%) were kept at 100 °C for 12 hours to remove moisture. These raw materials were weighed based on the chemical formula and then mixed via planetary ball mill using alcohol as a dispersion medium for 24 hours. After drying, the mixture was pre-fired at 850 °C for 4 hours and ball-milled for 24 hours again. The sieved powders were filled in a stainless-steel mold for a pre-compaction and then pressed into discs with a radius of 5 mm by a cold isostatic pressing facility at a pressure of 200 MPa for 3 min. Eventually, the samples could be obtained after densification at 1120 °C-1160 °C for 4-6 hour. In addition, the ceramic tapes based on KNN-0.20 were fabricated using a viscous polymer process (VPP), starting from pre-sintered powders. The calcined KNN-0.20 powders were mixed thoroughly with 38wt.% polyvinyl alcohol (PVA), followed by repeated rolling. Subsequent removal of PVA at 600 °C for 24 h enabled the production of KNN-0.20 ceramics with thickness about 40 µm through sintering at 1050 °C~1080 °C for 2 hours.

Characterization

The X-ray diffraction (XRD) was carried out on the D8 Advanced Diffractometer (Cu Kα radiation) to get the phase structures of KNN-*x* ceramics. The scanning electron microscopy (SEM) images were obtained using SEM (S-4800, Hitachi, Japan) to study the microstructures of the samples. The Nano-Measure software describes the average grain sizes of all the samples. The dielectric characteristics of the samples coated with silver electrodes were measured by an LCR analyzer (E4980A, Agilent, USA) in a temperature range from -190 °C to 500 °C with a heating rate of 3 °C/min and a frequency range from 1 kHz to 1 MHz. The ferroelectric tester (Premier II, Radiant, USA) was adopted to indicate the ferroelectric performances of the samples with an Au electrode of 3.14 mm² (all

prepared samples were sanded and smoothed to the thickness of about 70 μ m ~80 μ m). The forbidden band widths were acquired by the ultraviolet and visible (UV-vis) absorption spectra (Cary 5000, USA). The charge/discharge performance of samples with a thickness of 80 μ m were performed using a commercial charge-discharge device (CFD-001, Gogo Instruments Technology, Shanghai, China). The dynamic response of the domain to the external electric fields was investigated by piezo-response force microscopy (PFM) (MFP-3D, Asylum Research, USA), the samples were well polished using diamond suspension before PFM measurements. The ceramic impedance characteristics (DMS-1000, Partulab Technology Co., Ltd.) were tested at the frequency range of 0.1 Hz-5 MHz and temperature range of 220 °C-300 °C, the stimulus voltage is 20 mV and stabilization time is 5 min under tested environment. The HAADF atomic-scale images were acquired using an atomic-resolution STEM (aberration-corrected Titan Themis G2 microscope) and processed by 2D Gaussian fitting in MATLAB scripts to evaluate the polarization vector, magnitude, and angle maps.



Fig. S1 The pictures of microstructure evolution of KNN-x (x=0.1, 0.15, 0.25) system at different temperatures. The gray color represents the paraelectric phase, the other colors distinguish the ferroelectric domains with different orientations.



Fig. S2 (a) Unipolar *P-E* loops of KNN-*x* ceramics under critical electric fields; (b) Corresponding W_{rec} and η values calculated by *P-E* loops; (c) Weibull distribution of the breakdown strength for KNN-*x* ceramics; (d) Unipolar *P-E* loops of KNN-0.2 ceramic with 600 kV/cm at different frequencies; (e) Unipolar *P-E* loops KNN-0.2 ceramic with 600 kV/cm at different temperatures; (f) Under-damped discharge waveforms for the KNN-0.2 ceramic at different electric fields; (g) Over-damped discharge waveforms for KNN-0.2 ceramic at different electric fields; (h) Underdamped discharge waveforms at different temperatures under 600 kV/cm for KNN-0.2 ceramic; (i) Over-damped discharge waveforms at different temperatures under 600 kV/cm for KNN-600 kV/cm for KNN-0.2 ceramic.



Fig. S3 XRD patterns of the KNN-*x* ceramics.



Fig. S4 Temperature dependence of the dielectric permittivity (ε') and dielectric loss (tan δ) at 1 kHz~1 MHz for the KNN-*x* ceramics from -190 °C to 500 °C: (**a**) *x*=0 (**b**) *x*=0.10 (**c**) *x*=0.15 (**d**) *x*=0.25; (**e**) Temperature dependence of the dielectric permittivity (ε') and dielectric loss (tan δ) measured in the range of -190 °C to 500 °C at a fixed frequency of 1 MHz for KNN-*x* ceramics; (**f**) The degree of relaxation (γ) for KNN-*x* ceramics at 1 MHz.



Fig. S5 Vogel-Fulcher fit diagrams and $1000/\epsilon'-T$ plots for KNN-*x* ceramics: (**a**, **b**) *x*=0.10, (**c**, **d**) *x*=0.15, (**e**, **f**) *x*=0.20, (**g**, **h**) *x*=0.25.



Fig. S6 Out-of-plane PFM amplitude images of KNN-*x* ceramics: (**a**) x=0 (**b**) x=0.20; Out-of-plane PFM amplitude images after polarization with different voltages and relaxation durations (**c**) (**d**) KNN ceramic (**e**) (**f**) KNN-0.2 ceramic.



Fig. S7 (a) HADDF image of KNN-0.2 and (b) Lattice fringes viewed from the $[100]_c$ zone axis; (c) SAED pattern of KNN-0.2 ceramic; The element distribution maps of (d) K (e) Bi (f) Al (g) Na (h) Nb (i) Hf (j) Ni (k) Sr (l) Ta; (m) Polarization angle distribution along $[100]_c$; (n) Polarization magnitude distribution along $[100]_c$.



Fig. S8 (a) Absorption spectrum for KNN-*x* ceramics; (b) Leakage current density of KNN-*x* ceramics under different electric fields at room temperature; Complex impedance from 220 °C to 300 °C for (c) x=0 (d) x=0.1 (e) x=0.2; Combined -Z" and M" plots under 300 °C for (f) x=0 (h) x=0.1; Arrhenius fitting of the grain and the grain boundary for (g) x=0 (i) x=0.1.



Fig. S9 SEM images of the KNN-x ceramics: (a) x=0 (b) x=0.10 (c) x=0.15 (d) x=0.20 (e) x=0.25 (f) Average grain sizes of KNN-x ceramics; The statistics of grain size distribution for KNN-x ceramics: (g) x=0 (h) x=0.10 (i) x=0.15 (j) x=0.20 (k) x=0.25.



Fig. S10 Electric field distribution and electrical tree evolution for (**a**) KNN-0.1 ceramic and (**b**) KNN-0.2 ceramic at 600 kV/cm.

Phase-Field Simulations

A crystal considering cubic (C) to tetragonal (T) to orthorhombic (O) ferroelectric transition with defect doping concentration x=0-0.25 has been carried out in phase-field simulations. The total free energy of the ferroelectric system can be described as:

$$F = \int_{\mathcal{V}} (f_{\text{bulk}} + f_{\text{grad}} + f_{\text{couple}}) d\mathcal{V} + \int_{\mathcal{V}} (f_{\text{elas}} + f_{\text{elec}}) d\mathcal{V}$$
(S1)

where f_{bulk} represents the bulk free energy density,

$$f_{\text{bulk}} = \alpha_1 (P_1^2 + P_2^2 + P_3^2) - \alpha_{11} (P_1^2 + P_2^2 + P_3^2)^2 + \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_1^2 P_3^2)$$
$$+ \alpha_{112} (P_1^4 P_2^2 + P_2^4 P_3^2 + P_1^4 P_3^2 + P_1^2 P_2^4 + P_2^2 P_3^4 + P_1^2 P_3^4) + \alpha_{113} (P_1^2 P_2^2 P_3^2)$$
(S2)

where α_{ij} is the coefficient and depends on concentration and temperature.

$$f_{\text{gradient}} = \frac{1}{2} G_{11} [(P_{1,1})^2 + (P_{1,2})^2 + (P_{1,3})^2 + (P_{2,1})^2 + (P_{2,2})^2 + (P_{2,3})^2 + (P_{3,1})^2 + (P_{3,2})^2 + (P_{3,3})^2]$$
(S3)

where f_{grad} represents the gradient energy density. G_{11} is the gradient energy coefficient. f_{couple} represents the dipole effect caused by doping.

 $f_{\text{couple}} = -\int d^3x \sum_{i=1,2,3} P_i(x) \cdot \varphi_{\text{loc}}(x), \text{ where } \varphi_{\text{loc}}(x) \text{ is dipolar field created by doping,}$ and is assumed to distribute randomly and doesn't change under cooling. f_{elas} is the long-range elastic interaction energy densities and f_{elec} is the electrostatic interaction energy densities. $f_{\text{elas}} = \frac{1}{2} c_{ijkl} e_{ij} e_{kl} = \frac{1}{2} c_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0) (\varepsilon_{kl} - \varepsilon_{kl}^0), \text{ where } c_{ijkl} \text{ is the elastic constant tensor, } \varepsilon_{ij} \text{ the total strain, } \varepsilon_{ij}^0 \text{ the electrostrictive stress-free strain, i.e., } \varepsilon_{kl}^0 = Q_{ijkl} P_k P_l.$ $f_{\text{elec}} = f_{\text{diople}} + f_{\text{depola}} + f_{\text{appl}}, \text{ where } f_{\text{dipole}} \text{ is the dipole-dipole interaction caused by polarization, } f_{\text{depola}} \text{ the depolarization energy density and } f_{\text{appl}} \text{ the energy density caused by applied electric field. The temporal evolution of the spontaneous polarization field (P) can be obtained by solving the time-dependent Ginzburg-Landau (TDGL) equation: <math>\frac{dP_i(x,t)}{dt} = -M \frac{\delta F}{\delta P(X,t)}, i=1, 2, 3, \text{ where } M \text{ is } M \text{$

the kinetic coefficient, F is the total free energy, and t is time [1-4].

First-order reversal curve

The FORC distribution is derived from a series of FORC loops and the Preisach density ρ (α , β) calculated by the following equation:

$$\rho(\alpha,\beta) = \frac{1\partial P^2(\alpha,\beta)}{2 \quad \partial \alpha \partial \beta}$$
(S4)

where ρ (α , β) is the polarization of the FORC loop, α is the reversal electric field, and β is the actual electric field. The Preisach density represents the density distribution of the ideal 'hysteron' and provides the information of the local switching behavior. In this work, we set E_{max} =60 kV/cm, $\Delta \alpha$ = $\Delta \beta$ =4 kV/cm and 60 FORC loops were measured.

Finite Element Simulation of Dielectric Breakdown

According to the structural model proposed by Randall et al., the dielectric constant of the grain and grain boundary can be calculated with the macroscopic dielectric constant of the ceramics by the following formula [5-6]:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_g} + \frac{1}{k\varepsilon_{gb}}$$
(S5)

where ε' , $\varepsilon'_{gand} \varepsilon'_{gb}$ represent the dielectric constant of the ceramics, grain and grain boundary, respectively. k is the ratio of grain size and grain boundary thickness. Based on the above formula and the measured macroscopic dielectric constant and average grain size of KNN-0.1 and KNN-0.2 ceramics, the calculated dielectric constant of the ceramic grain is 1560 and 1220 for KNN-0.1 and KNN-0.2 ceramics.

Simulation of Dielectric Breakdown Process on Microscale: The development characteristics of breakdown paths in the process of breakdown can be simulated by the finite element method using the breakdown model, as illustrated by the following formula:

$$p(i, j \rightarrow i'j') = A(\varphi_{i',j'})^m / \sum (\varphi_{i',j'})^m + B(\varphi_{i',j'}) / \varphi_0 + C$$
(S6)

where *p* is the grown probability of electrical tree paths, (i, j) and (i', j') represent the coordinates of discrete lattice system in finite element model, φ_0 is the threshold electric potential evaluating the minimum voltage driving electrical tree development, m denotes the fractal dimension whose value is 3 in this work. The first term of the right polynomial manifests the growth direction of electrical trees, the second term reflects the growth difficulty degree of electrical trees, and the last one is related to the dielectric properties of materials. The values of A, B, and C are the weighting coefficients of each term, respectively.

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