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# Giant dielectric breakdown strength together with ultrahigh energy density in ferroelectric bulk ceramics via layer-by-layer engineering

# Supporting information

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## 1. The philosophies of layered materials design

In layer-by-layer structured ceramics, each ceramic layer can be considered as an individual capacitor. All these capacitors are connected in series as seen in Figure S1. Supposing there are only two different layers with the dielectric permittivity and the thickness of $\varepsilon_1$, $d_1$ and $\varepsilon_2$, $d_2$, respectively. The overall thickness ($d$) is equal to $d_1 + d_2$. When applying a voltage U, the divided voltage on the first layer can be written as

$$U_1 = \frac{C_2}{C_1 + C_2} \cdot U \quad (1)$$

according to the voltage divider rule in capacitors,[1] where $C_1 = \varepsilon_1 S/d_1$ and $C_2 = \varepsilon_2 S/d_2$ are capacitances of the first layer and the second layer, respectively, with

*S* representing the electrodes area. The electric field in the first layer ($E_1$) and the applied electric field ($E$) are calculated as $E_1=U_1/d_1$ and $E=U/d$. Therefore, the ratio of the first layer and the applied electric field is described by

$$\frac{E_1}{E}=\frac{U_1 d}{U d_1}=\frac{\varepsilon_2 S/d_2}{\varepsilon_1 S/d_1+\varepsilon_2 S/d_2}\cdot\frac{d}{d_1} \quad (2)$$

The formula (2) can be further rearranged as

$$\frac{E_1}{E}=\frac{1}{\frac{\varepsilon_1}{\varepsilon_2}\cdot\frac{d_2}{d}+\frac{d_1}{d}} \quad (3)$$

From formula (3), if $\varepsilon_1<\varepsilon_2$, then $E_1>E$, otherwise, $E_1<E$, which indicates that the local electric field is concentrated in dielectric layer with the smaller dielectric permittivity. The thinner the small permittivity layer is, the higher the local electric field concentrated.

Let's take a close look at composition modification improved $0.87BaTiO_3$-$0.13Bi(Zn_{2/3}(Nb_{0.85}Ta_{0.15})_{1/3})O_3$ (BTBZNT)[2] ceramics and structure modification improved $BaTiO_3$@3wt% $Al_2O_3$, 1wt% $SiO_2$ (BTAS)[3] ceramics. The room-temperature dielectric permittivity of BTAS is smaller than that of BTBZNT (see Figure 4(a)). The dielectric permittivity difference between BTAS and BTBZNT is even larger under the high applied electric field due to the stronger *P*-*E* nonlinear of BTAS ceramics (see Figure 4(b)). As a result, the local electric field is concentrated in BTAS layers. Meanwhile, the BTAS layers possess a higher breakdown strength and can prevent the retard the propagation of breakdown paths, resulting in the enhanced

breakdown strength of these layer-by-layer structured ceramics. It is known to all that the breakdown strength of dielectric materials is highly related to its thickness.[4-6] A thinner layer will lead to a higher breakdown strength but a severe local-electric-field concentration at the same time. By the comprehensive consideration of dielectric breakdown strength and the co-sintering condition of BTAS and BTBZNT layers, The layer thickness of BTAS layer (~13 $\mu$m, before sintering) is designed a little thinner than BTBZNT layer (~17 $\mu$m, before sintering).

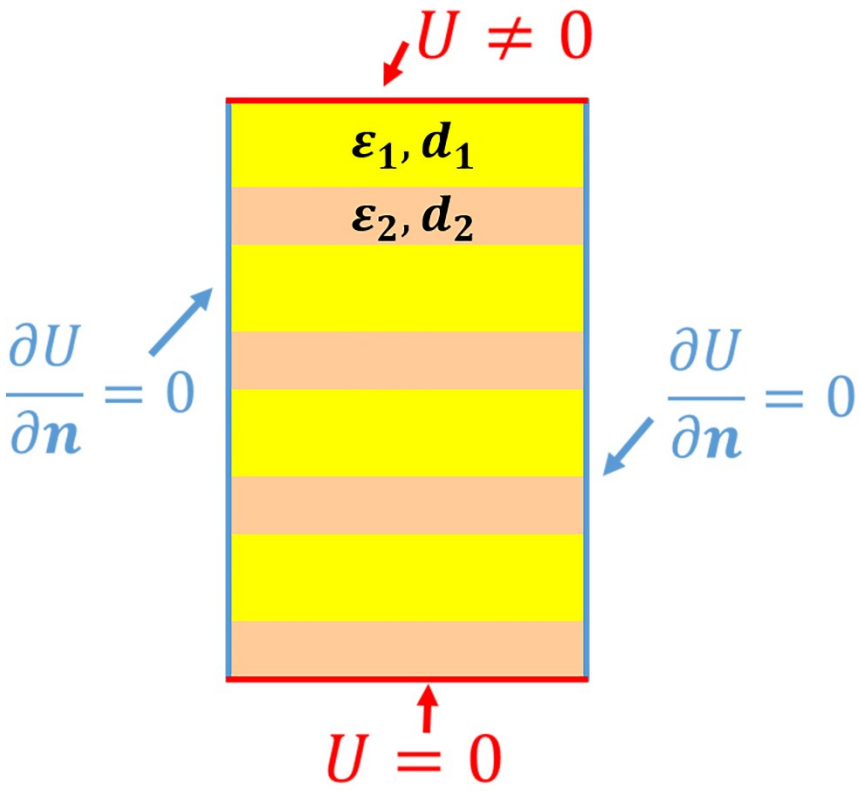


Figure S1. Schematic diagram of layer-by-layer structured ceramics and the loading setup in phase-field breakdown model.

**2. Phase-field breakdown model**

To analyze the mechanism for the enhanced breakdown strength caused by the layer-by-layer structure designing, a scalar spatially and temporally dependent damage field

$s$ ($x$, $t$) is introduced to characterize the breakdown process of these ceramics with layer-by-layer structures[7-9]. The value of $s$ varies from 1 to 0, representing the intact state and the fully damaged state, respectively. For any other intermediate state, the permittivity is interpolated by

$$\varepsilon(s) = \frac{\varepsilon_0}{f(s) + \eta}, \tag{4}$$

where $f(s) = 4s^3 - 3s^4$ and $\varepsilon_0$ is the initial permittivity. Breakdown happens if the process decreases the total potential energy of the system,

$$\Pi[s,\phi] = \int_{\Omega} \left[W_{es}(E,s) + W_d(s) + W_i(\nabla s)\right] dV, \tag{5}$$

where $W_{es}(E,s) = -\frac{\varepsilon}{2} E \cdot E$ is the complementary electrostatic energy per unit volume, $W_d(s) = W_c[1 - f(s)]$ is the breakdown energy function with $W_c$ representing the critical density of electrostatic energy, $W_i(\nabla s) = \frac{\Gamma}{4} \nabla s \cdot \nabla s$ is the gradient energy term to regulate sharp phase boundaries. Notably, the material parameter $\Gamma$ is approximately the breakdown energy. According to linear kinetic law: $\partial s/\partial t = -m\delta\Pi/\delta s$, the evolution equation for breakdown variable $s$ can be obtained after substituting in detailed forms of the energy functions:

$$\frac{1}{m}\frac{\partial s}{\partial t} = \frac{\varepsilon'(s)}{2} \nabla\phi \cdot \nabla\phi + W_c f'(s) + \frac{\Gamma}{2} \nabla^2 s. \tag{6}$$

Here, mobility $m$ is a material parameter that indicates the speed of breakdown propagation in layer-by-layer structured ceramics. By normalizing all lengths by $l$, energy densities by $W_c$, time by $l^2/m\Gamma$, and electric potential by $\sqrt{\Gamma/\varepsilon_0}$, the final normalized governing equations of dimensionless form can be written as:

$$\bar{\nabla} \cdot \left[ \frac{1}{f(s)+\eta} \bar{\nabla} \bar{\phi} \right] = 0, \tag{7}$$

$$\frac{\partial s}{\partial \bar{t}} = - \frac{f^{'}(s)}{2[f(s)+\eta]^2} \bar{\nabla} \bar{\phi} \cdot \bar{\nabla} \bar{\phi} + f^{'}(s) + \frac{1}{2} \bar{\nabla}^2 s \,, \tag{8}$$

in which the corresponding quantities are symbolized with over-bars. The dielectric breakdown behavior of layer-by-layer structured ceramics can be simulated by implementing the normalized governing equations (7) and (8) into COMSOL Multiphysics platform.

## 3. Hysteresis loops and current-electric-field relations

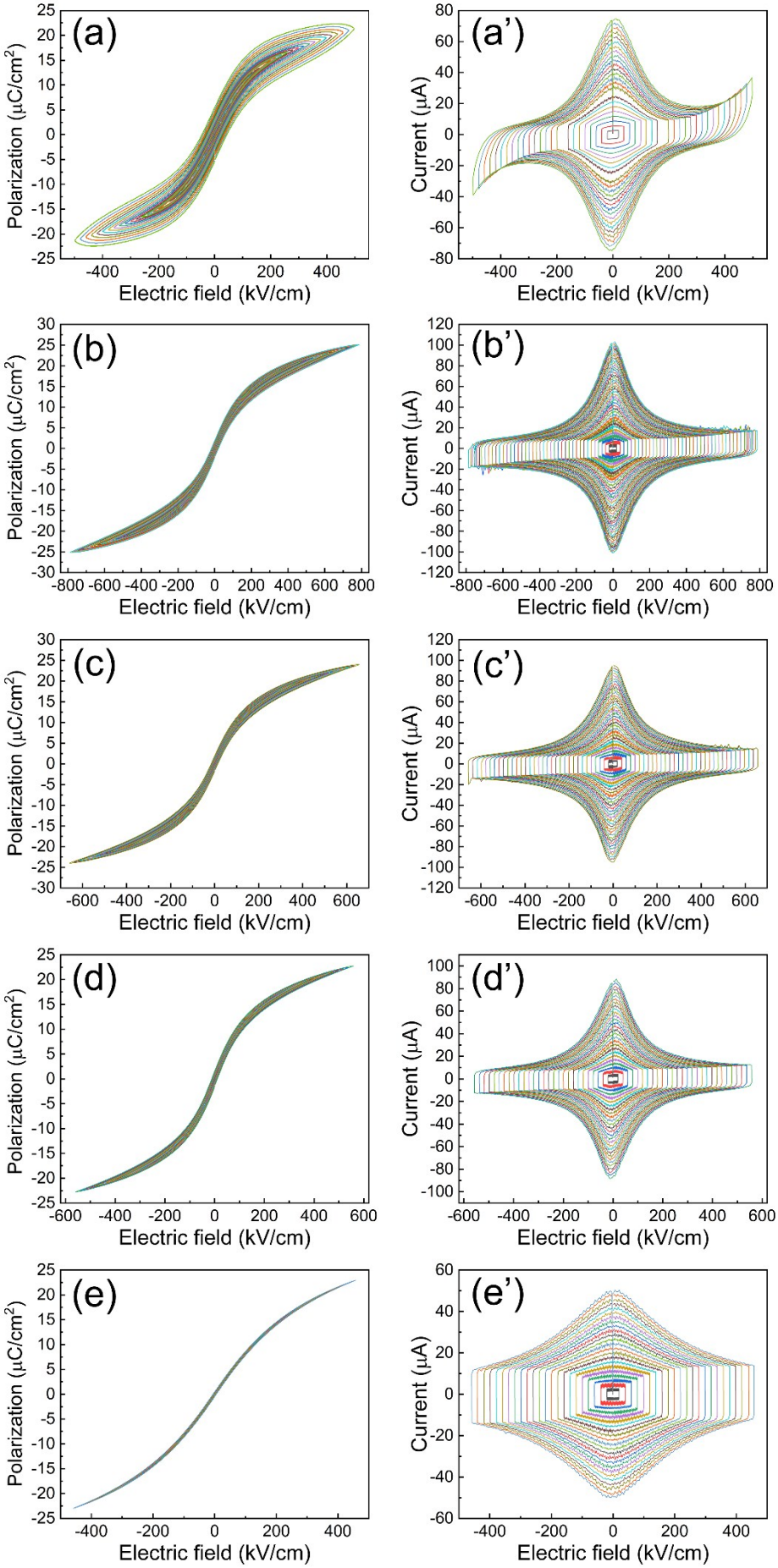
(a)
Polarization (μC/cm²)
Electric field (kV/cm)
(a')
Current (μA)
Electric field (kV/cm)
(b)
Polarization (μC/cm²)
Electric field (kV/cm)
(b')
Current (μA)
Electric field (kV/cm)
(c)
Polarization (μC/cm²)
Electric field (kV/cm)
(c')
Current (μA)
Electric field (kV/cm)
(d)
Polarization (μC/cm²)
Electric field (kV/cm)
(d')
Current (μA)
Electric field (kV/cm)
(e)
Polarization (μC/cm²)
Electric field (kV/cm)
(e')
Current (μA)
Electric field (kV/cm)

Figure S2. (a) to (e) Hysteresis loops of all these five samples, (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, measured under various applied electric fields at 1Hz. (a') to (e') The current-electric-field relation of all these five samples corresponding to (a) to (e).

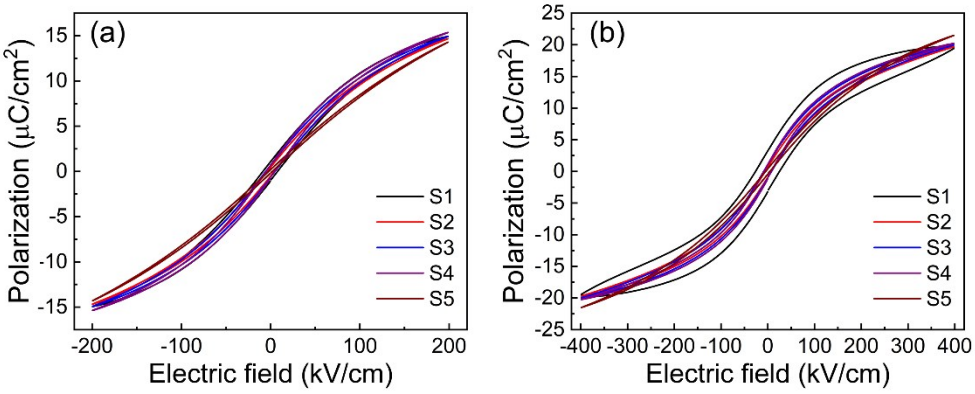


Figure S3. Hysteresis loops of all these five samples measured under the applied electric field of (a) 200 kV/cm and (b) 400 kV/cm at 1 Hz.

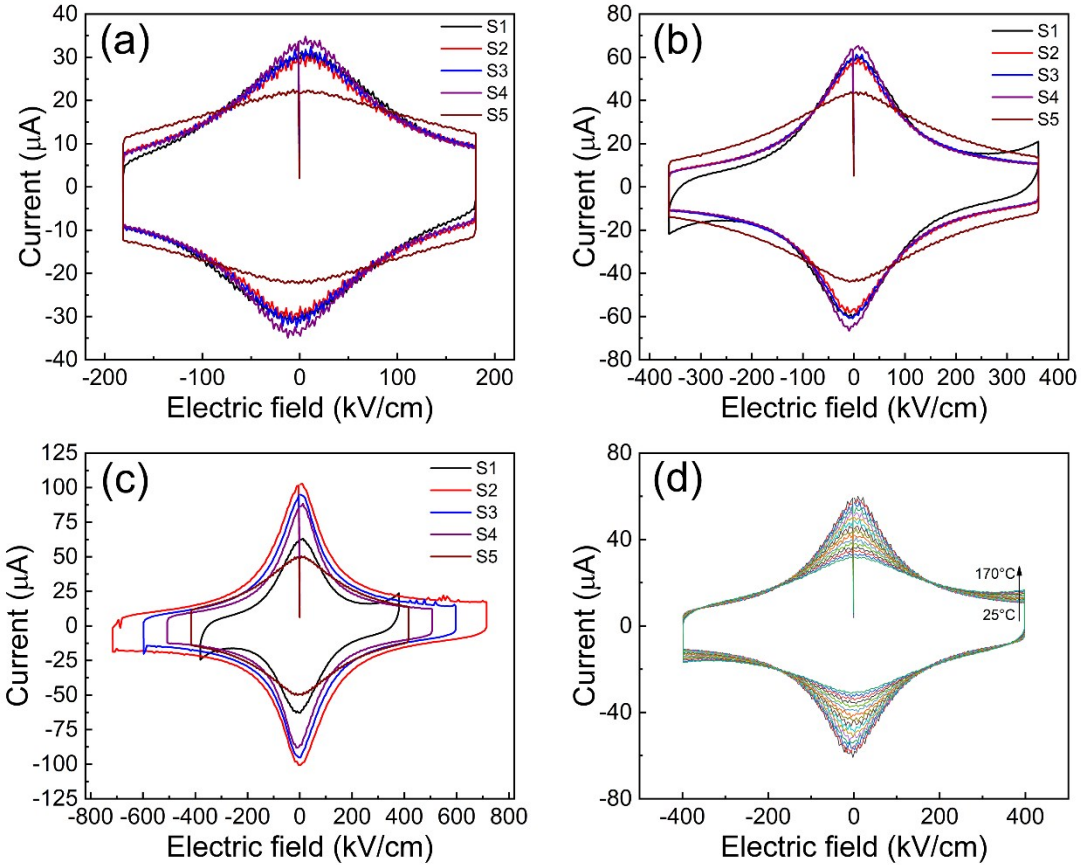


Figure S4. (a) and (b) The current-electric-field relation of all these five samples corresponding to (a) and (b) in Figure S2. (c) The current-electric-field relation of all these five samples corresponding to Figure 4(c). (d) The temperature-dependent current-electric-field relation of sample S2 corresponding to Figure 5(a).

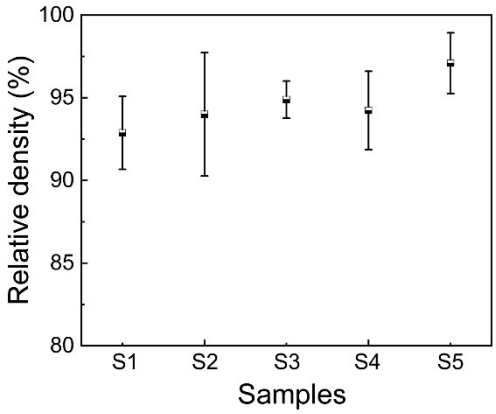


Figure S5. The relative density of all these five samples.

**4. Two-step sintering method**

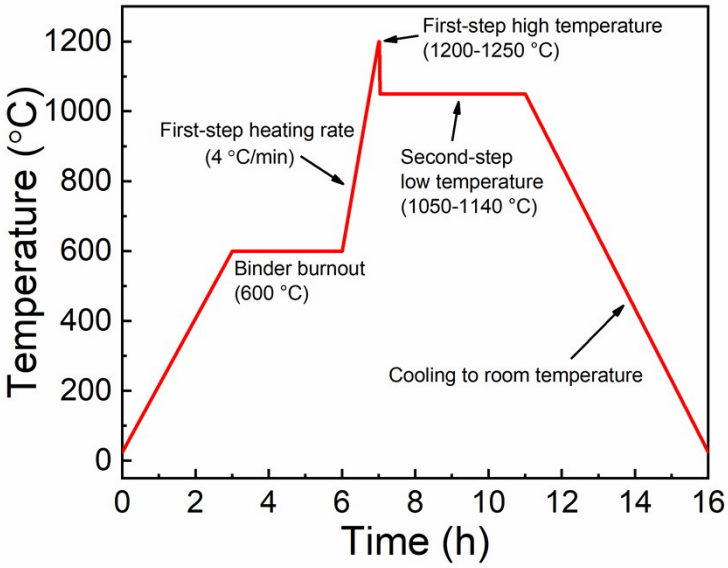


Figure S6. The two-step sintering schedule of these five layer-by-layer structured ceramics.

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