Optimizing the energy storage performance of NaNbO$_3$ ceramics by rare-earth-based composite perovskite Sm(Mg$_{0.5}$Zr$_{0.5}$)O$_3$ modification

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1. Test instrument information

X-ray powder diffraction (XRD, Model X'Pert PRO; PANalytical, Almelo, Netherlands) with Cu Kα radiation (λ = 0.15406 nm) was used to analyze the phase structures of the samples. A scanning electron microscope (Model JSM6380-LV, JEOL, Tokyo, Japan) was used to observe the natural surface microstructures of the samples. The relative permittivity and loss tangent of the ceramics, which were coated with silver electrodes on both sides, were measured using a precision impedance analyzer (Model 4294A, Hewlett-Packard Co, Palo Alto, CA) in the temperature range of -160°C to 180°C at a heating rate of 2°C/min. To investigate the energy storage properties further, the sintered sample was polished to a thickness of 0.15 ± 0.01 mm and coated with sliver paste with a diameter of 2 mm (the area was 3.14 mm^2). The temperature was raised to 700°C and then maintained for 30 min at a heating rate of 3°C/min, and a simple parallel plate capacitor was made for the *P-E* loop test - FE material parameter tester (RT66, Radiant Technologies, NM, USA). The Raman shifts were measured at room temperature using a Raman tester (XDR, Thermo Fisher Scientific, USA). The dielectric breakdown strength (*E*$_b$) was

measured at room temperature using an S-4(RK2671AM) voltage-withstanding test device. A dielectric charge test system (CFD-003, TG Technology, Shanghai, China) was used to measure the charging and discharging performances. The thicknesses and silver electrode areas of the samples used for *P–E* testing are listed in Table S1.

2. Table

Table S1. Electrode thickness and area of P-E test samples

x	0.05	0.08	0.12	0.15
Sample thickness (um)	95	98	107	107
Electrode area (cm^2)	0.0314	0.0314	0.0314	0.0314

Table S2. Sample density of each component

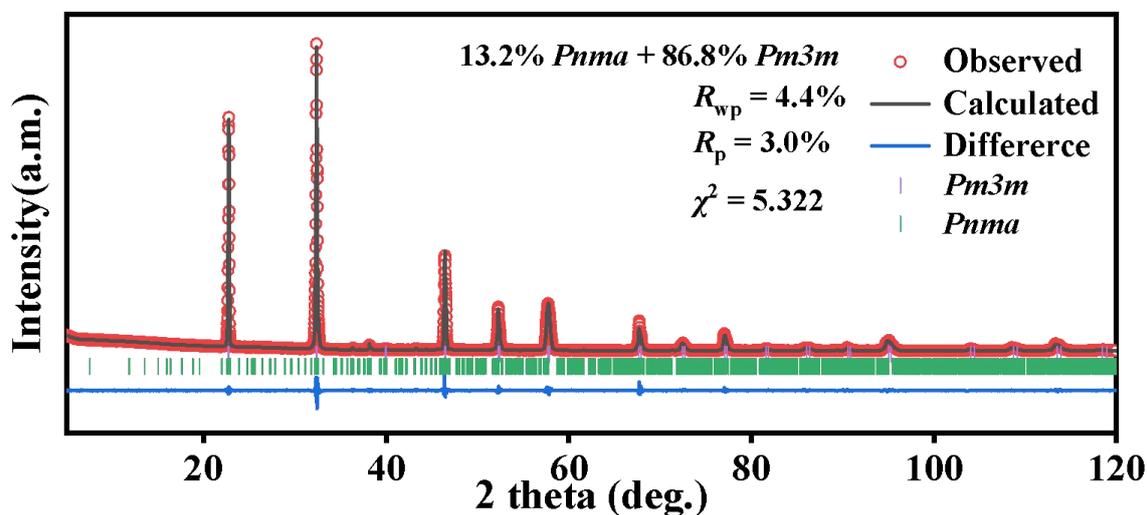| x	0.05	0.08	0.12	0.15
Temperature (°C)	1,360	1,350	1,340	1,340
Density (g/cm^3)	4.66	4.70	4.77	4.82

3. Figure

Figure S1. XRD refinement of 0.10SMZ component.
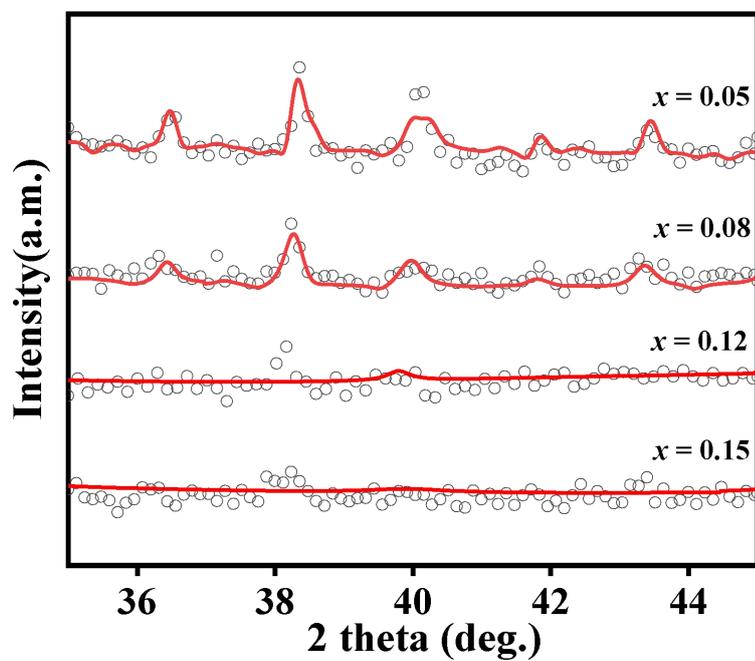
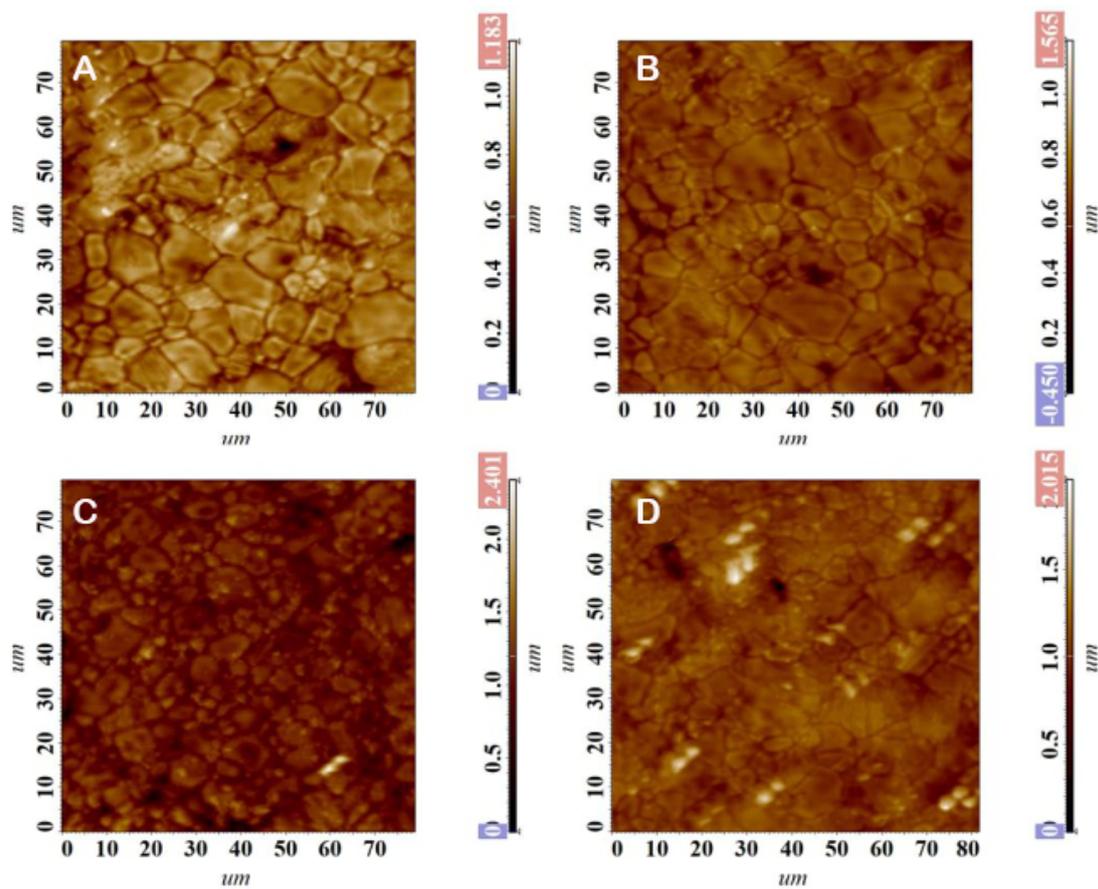**Figure S2.** XRD refinement result of the *x*SMZ component at 35° ~ 45°.
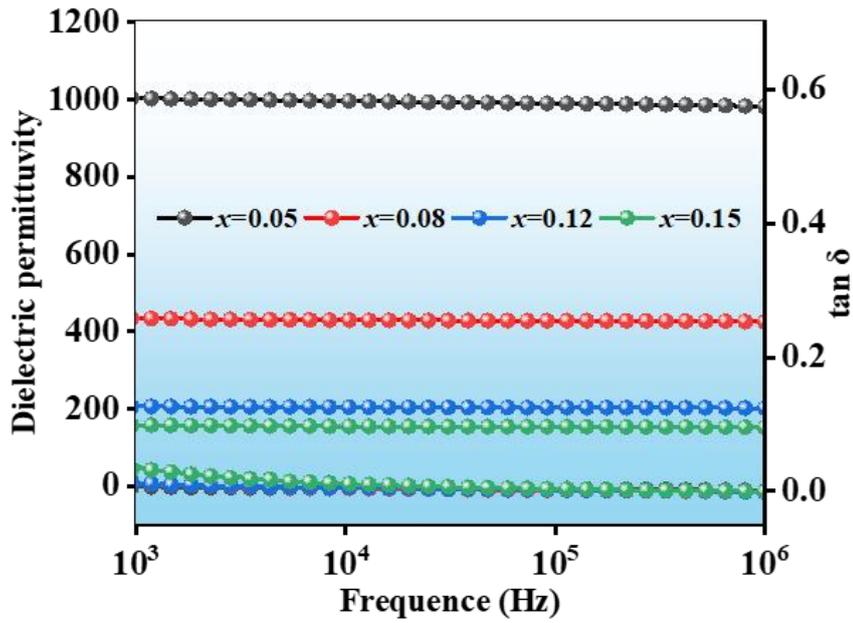

Figure S3. AFM image of NN-SMZ ceramics (A) ~ (D).

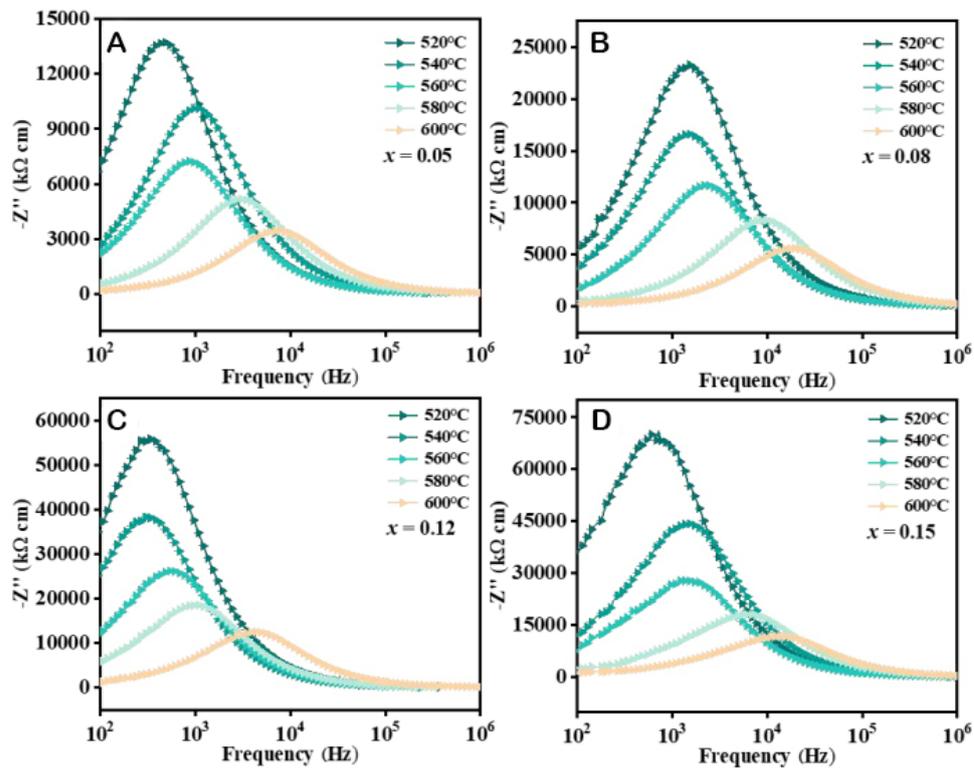**Figure S4.** *x*SMZ ceramic dielectric constant versus frequency diagram.

Figure S5. The evolution of -*Z*″ as a function of frequency with increasing temperature (A) ~ (B).
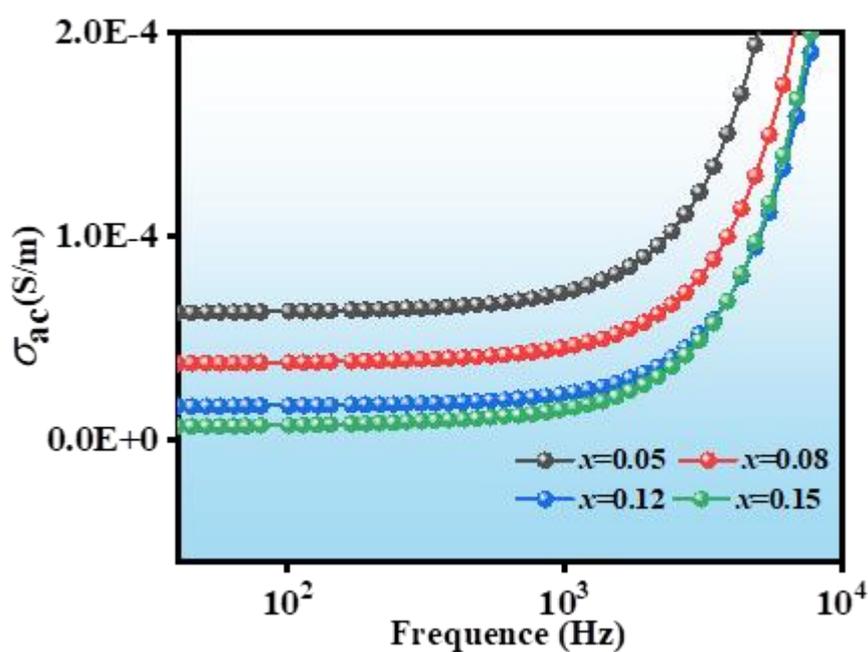
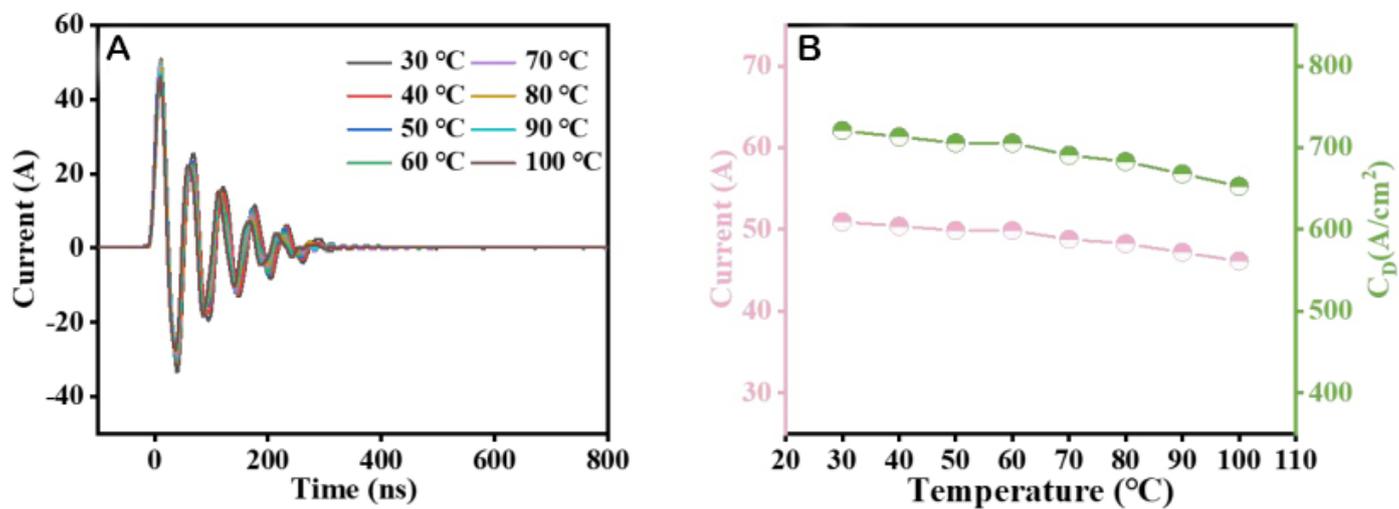**Figure S6.** The relationship between AC conductivity and frequency change

Figure S7. (A) Over-damped discharge current curves of 0.08SMZ ceramics at different temperatures. (B) The changes of I_{max}, C_D under different conditions.
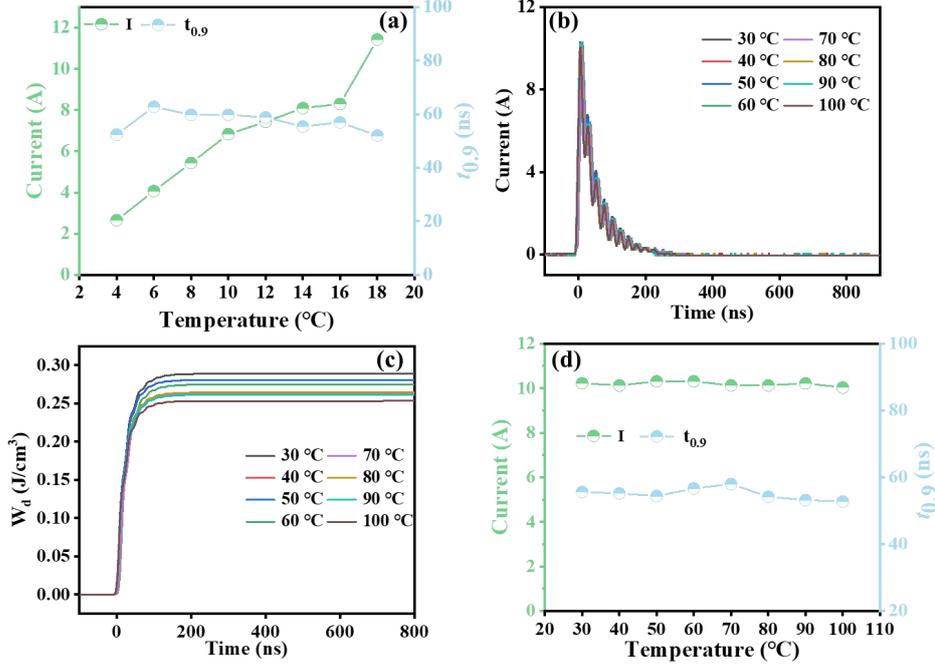
Figure S8. (A) $t_{0.9}$ and I_{max} of overdamped charge-discharge at various electric fields. (B) ~ (C) Over damper discharged current curves of the 0.08SMZ ceramics at various temperatures. (D) $t_{0.9}$ and I_{max} of overdamped charge- discharge at various temperatures.

4. Formula

In general, the recoverable energy storage density of the sample is calculated using the following formula:

$$W_{rec} = \int_{P_r}^{P_{max}} E dP \tag{1}$$

W_{rec} is the recoverable energy storage density, P_{max} is the maximum polarization intensity, P_r is the residual polarization intensity, and E is the electric field.

To study the mechanism of breakdown strength enhancement of 0.08SMZ ceramics compared with NN ceramics, a scalar field $s(x, t)$ is introduced to characterize the breakdown state of the materials, where the value of s varies from 1 to 0, s = 1 represents the complete state, and s = 0 represents the complete breakdown state. Therefore, ε_r is a continuous function of the field variable s and can be expressed as:

$$\varepsilon(s) = \frac{\varepsilon_{\text{intact}}}{f(s) + \eta},$$

(2)

where $f(s) = 4s^3 - 3s^4$, $\varepsilon_{\text{intact}}$ represents the initial ε_r, and η is 0.001. Herein, for polycrystalline ceramics, including both grains and grain boundaries, the ε_r of the grain boundary (ε_{gb}) is assumed to be a linear distribution with increasing electric field, whereas that of the ferroelectric grain is assumed to be a nonlinear distribution. The relationship between the change in their ε_r and the electric field is described by the following formula:

$$\varepsilon_{ini}(E) = \begin{cases} \varepsilon_g(0)/(1+kE^2)^{2/3}, & \text{grain} \\ \varepsilon_{gb}, & \text{grain boundary} \end{cases}$$

(3)

where the k is the non-linear factor, with a value set to 0.01323. To quantitatively describe the dielectric breakdown behavior, the $\varepsilon_{\text{intact}}$ of 0.08SMZ ceramics was set to be: $\varepsilon_g(0)/\varepsilon_{gb}(0) = 10$, $\Gamma_g(0)/\Gamma_{gb}(0) = 0.1$. The theoretical model in this work is built by the following mathematical expression:

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

(4)

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

(5)