

Supplementary Information

Thermal-stability of the enhanced piezoelectric, energy storage and electrocaloric properties of lead-free BCZT ceramic

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S1. Experimental section

S1.1. Elaboration of BCZT ceramic

Lead-free $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ (BCZT) powder was prepared by the conventional solid-state reaction route. Barium carbonate (BaCO_3 , $\geq 99\%$, VWR Chemicals), calcium carbonate (CaCO_3 , $\geq 98.5\%$, VWR Chemicals), zirconium oxide (ZrO_2 , $\geq 99.5\%$, Merk) and titanium oxide (TiO_2 , $\geq 99.5\%$, VWR Chemicals) were used as starting materials. The stoichiometric amounts of the precursors were mixed in an agate mortar for 3 h using ethanol as a medium, then dried and calcined at $1300\text{ }^\circ\text{C}/12\text{ h}$ with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. Using 5 wt% of polyvinyl alcohol (PVA) as a binder, the calcined powders were uniaxially pressed into pellets of diameter about 12 mm and thickness about 0.8 mm. The pellets were first heated up at $800\text{ }^\circ\text{C}$ for 2 h to remove the binder and followed by sintering at $1350\text{ }^\circ\text{C}$ for 7 h.

S1.2. Characterisations

The room-temperature crystalline structure of BCZT ceramic was examined by the X-ray diffraction (XRD, Panalytical X-Pert Pro) under a step angle of 0.02° in the 2θ range from 10° to 80° using $\text{Cu-K}\alpha$ radiation ($\lambda \sim 1.5406\text{ \AA}$). Raman spectroscopy was also used to examine the structural properties change in BCZT ceramic from 0 to $150\text{ }^\circ\text{C}$. For this purpose, the BCZT sample was excited using the polarised radiation of an argon laser ($\lambda = 514.5\text{ nm}$) and registered using a Renishaw in Via Reflex spectrometer equipped with a Near-Excitation Tunable (NExT) filter for the analysis of the low-frequency spectral range down to 50 cm^{-1} . An optical microscope with a $\times 50$ objective was employed to focus the incident light as a $2\text{-}\mu\text{m}$ -diameter spot on the sample. For temperature-dependent micro-Raman measurements, a well-calibrated Linkam freezing stage with temperature stability of 0.1 K was used. To compare the spectra obtained at various temperatures, Bose-Einstein correction has been performed. The scanning Electron Microscopy (SEM, Tescan VEGA3) was performed at a voltage of 10 kV to analyse the sintered ceramic's surface morphology. The sample's grain size distributions were determined using ImageJ software, and the density of BCZT ceramic was evaluated using the Archimedes' method. The dielectric properties of gold-sputtered BCZT ceramic were measured by using a precision LCR Meter (Agilent, 4284A) equipped with Data Acquisition Switch Unit, a temperature chamber (Delta 9039) and a furnace (Nabertherm), in the frequency range of 1 kHz to 1 MHz . The polarisation-electric field ($P-E$) and the strain-electric field ($S-E$) hysteresis loops of the BCZT ceramic with a thickness of $310\text{ }\mu\text{m}$ were simultaneously measured by using an AixACCT TF 2000 Analyzer with

a SIOS Meßtechnik GmbH laser interferometer and a high-voltage amplifier (TREK model 609E-6) in a silicone oil bath. The hysteresis loops were measured using an excitation sinusoidal signal with a frequency of 10 Hz in the temperature range of 30-150 °C with a 5 °C step upon the heating cycle. The electrocaloric response was determined from the recorded P - E hysteresis loops at 10 Hz using the indirect Maxwell approach.

S2. Relaxor properties in BCZT ceramic

In the paraelectric phase, the ferroelectric materials obey the Curie-Weiss law, given in Eq. (S1).¹ The thermal-evolution of the inverse of ϵ_r at 1 kHz was fitted using the Curie-Weiss law and plotted in Fig. S1a. Where ϵ_r is the dielectric constant, T_0 is the Curie-Weiss temperature and C is the Curie-Weiss constant. The fitting results are gathered in Table S1.

$$\frac{1}{\epsilon_r} = \frac{T - T_0}{C} (T > T_0). \quad (S1)$$

Here $\Delta T_m = T_{dev} - T_m$ describes the degree of deviation of the ϵ_r from the Curie-Weiss law above T_C , where T_{dev} is the temperature at which ϵ_r starts to deviate from the Curie-Weiss law and T_m is the temperature at which ϵ_r reached the maximum. The Curie constant (C) value is in the order of 10^5 K, which indicates that the paraelectric to the ferroelectric phase transition of BCZT ceramic is of a displacive type such as in BaTiO_3 . These parameters are summarised in Table S1.

Moreover, the diffuseness associated with the FE-PE phase transition could be determined via the fit of the modified Curie-Weiss law as written in the Eq. (S2), the results are plotted in Fig. S1b.²

$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_m} = \frac{(T - T_0)^\gamma}{C} (1 < \gamma < 2). \quad (S2)$$

Where ϵ_m denotes the maximum dielectric constant and γ refers to the phase transition's degree of diffuseness. The limiting values $\gamma = 1$ and $\gamma = 2$ characterise the typical ferroelectric behaviour following the Curie Weiss law and the

ideal relaxor ferroelectric, respectively. Hence, BCZT ceramic exhibits a γ value of 1.74, and the estimated value of deviations ΔT_m is 32 °C, indicating a strong diffused phase transition.

Hanani et al.³ reported comparable values of 1.75 and 37 °C for γ and ΔT_m , respectively, for the same BCZT composition.

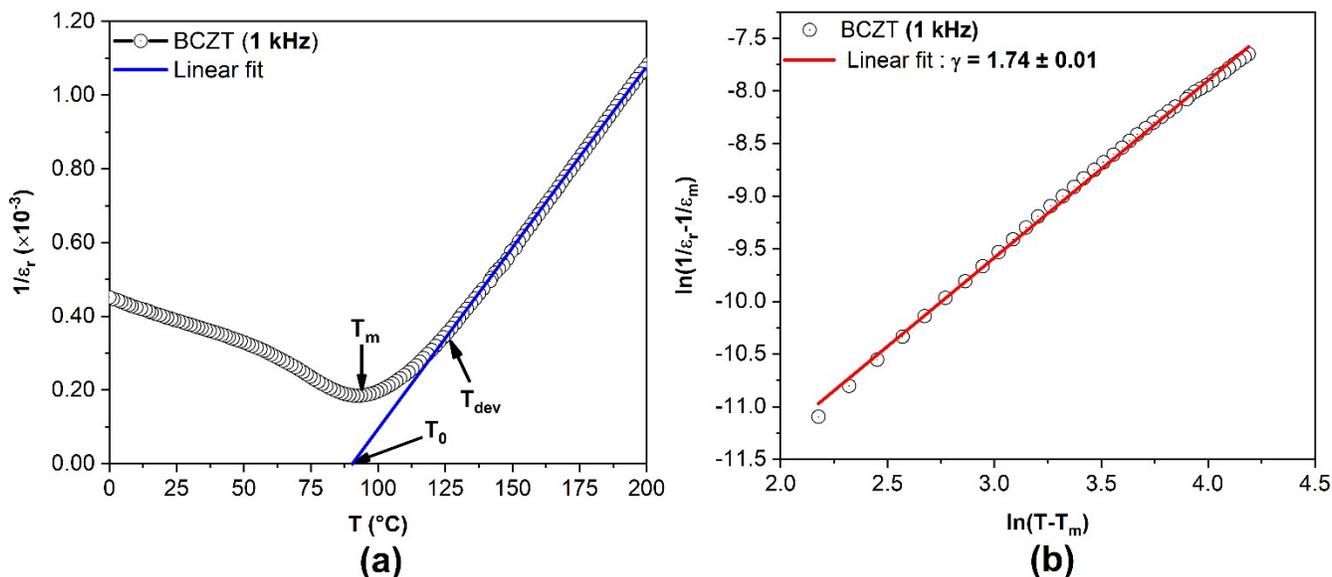


Fig. S1 Plots of the inverse ϵ_r as a function of temperature determining the Curie-Weiss constant C at 1 kHz and the inset shows the $\ln(1/\epsilon - 1/\epsilon_m)$ vs $\ln(T - T_m)$, determining the degree of diffuseness γ of the BCZT ceramic.

Table S1. Relaxor properties of BCZT sample at 1 kHz.

| | ϵ_r (at T_m) | $\tan\delta$ (at T_m) | $C \times 10^5$ (K) | T_0 (°C) | T_m (°C) | T_{dev} (°C) | ΔT_m (°C) | γ |
|------|-----------------------------|-----------------------------|------------------------|---------------|---------------|-------------------|----------------------|----------|
| BCZT | 5400 | 0.019 | 1.01 | 90.87 | 93.66 | 125.72 | 32.12 | 1.74 |

References

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