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Sufficiently optimized energy storage properties of the antiferroelectric ceramics by modulating the phase structure via constructing a novel binary composite

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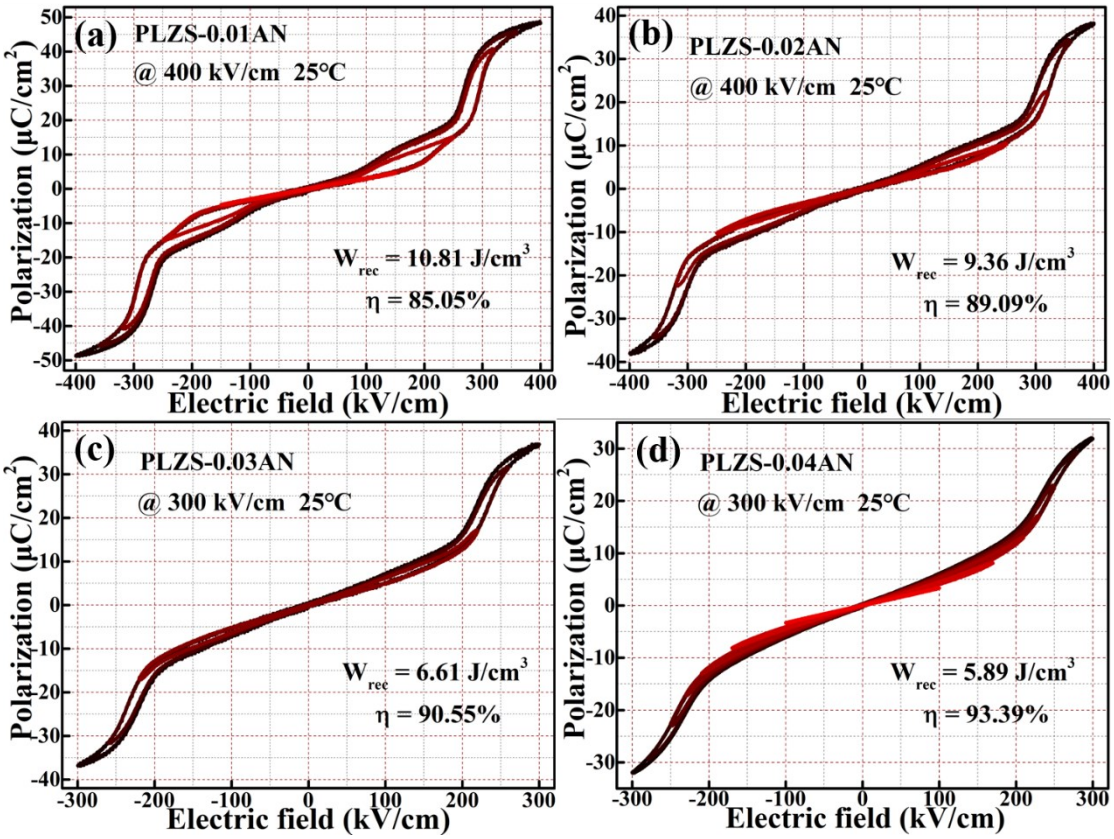

Figure S1 a)-d) The saturated P-E loops under each utmost electric field at room temperature for four compositions from AN1 to AN4 in proper sequence.

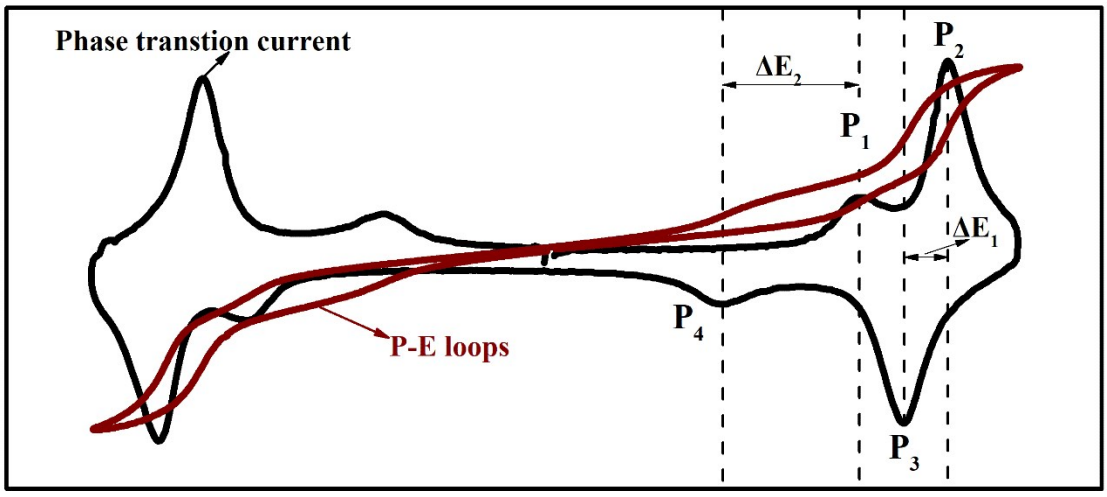

Figure S2 The schematic diagram of multiphase transition process under electric loading and the corresponding phase transition current.

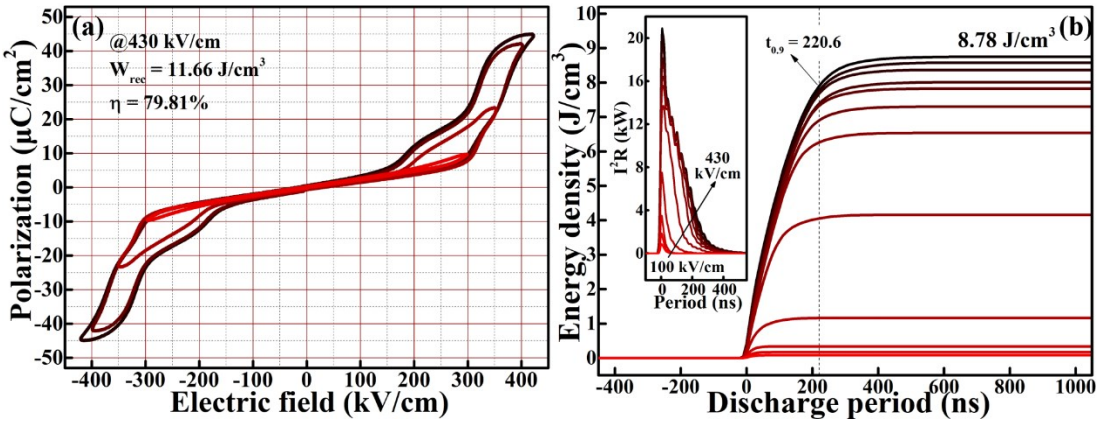

Figure S3 a) The saturated P-E loops under the electric field of 430 kV/cm at room temperature for the controlled composition of $(Pb_{0.97}La_{0.02})(Zr_{0.6}Sn_{0.4})O_3$. b) The corresponding over-damped (518 Ω) charge-discharge curves and the calculated discharge energy density.

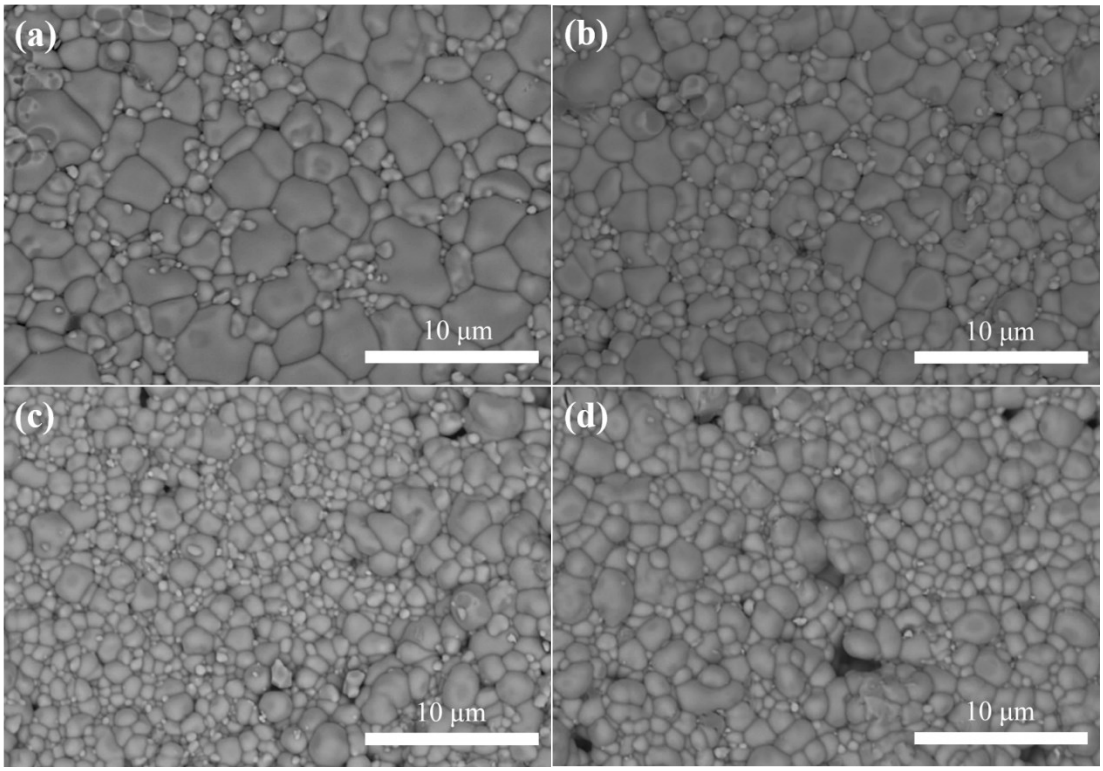

Figure S4 a)-h) The free-surface SEM images for all as-sintered samples without any heat treatment, from AN1 to AN4 in proper sequence.

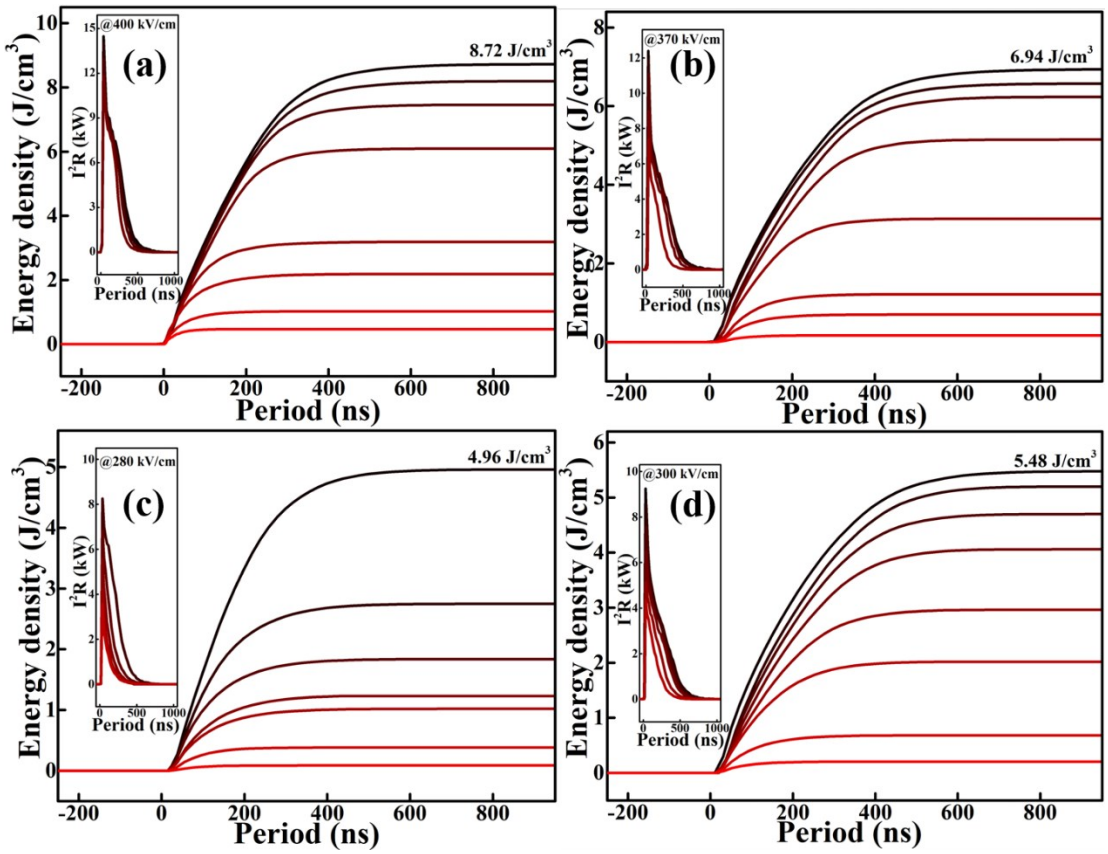

Figure S5 a)-d) The over-damped charge-discharge curves for the four compositions under each utmost DC bias at room temperature (950 Ω) from AN1 to AN4 in proper sequence.

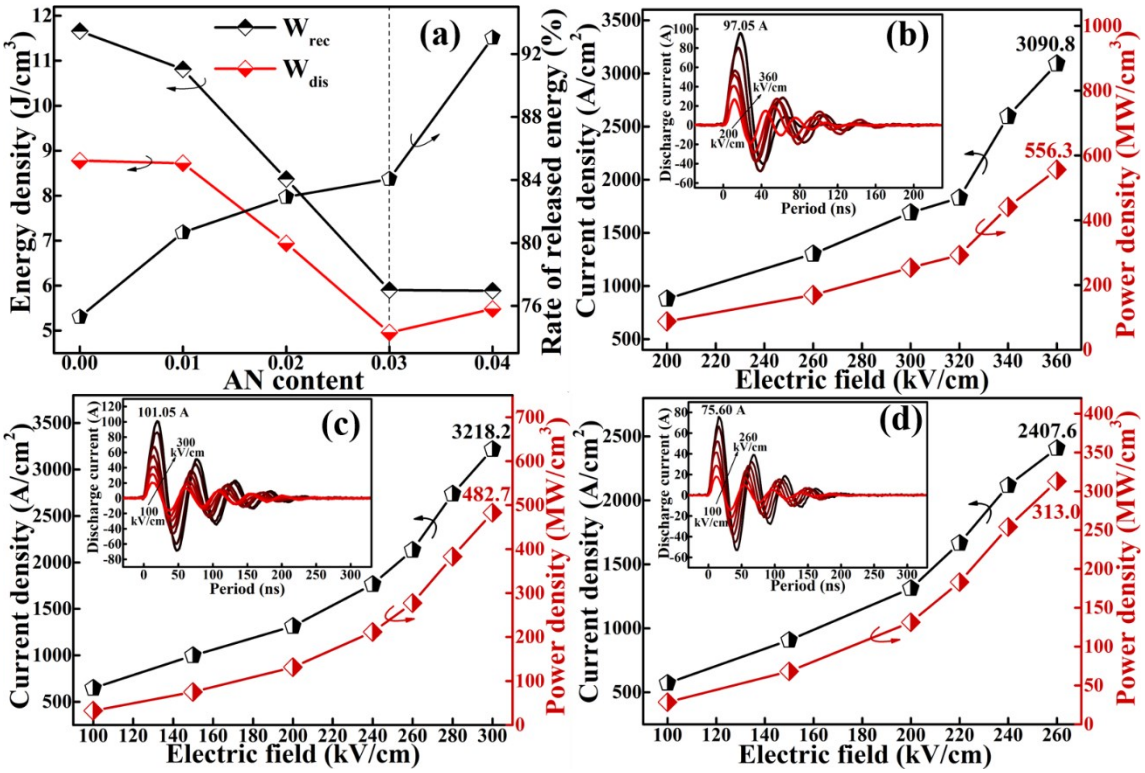

Figure S6 a) The statistical figure of the theoretically recoverable energy storage density, the corresponding discharge energy density at the same electric field and the energy utilization. b)-d) The underdamped charge-discharge curves, the corresponding calculated CD and PD as the function of external electric field for the sample AN1, AN2 and AN4, respectively.

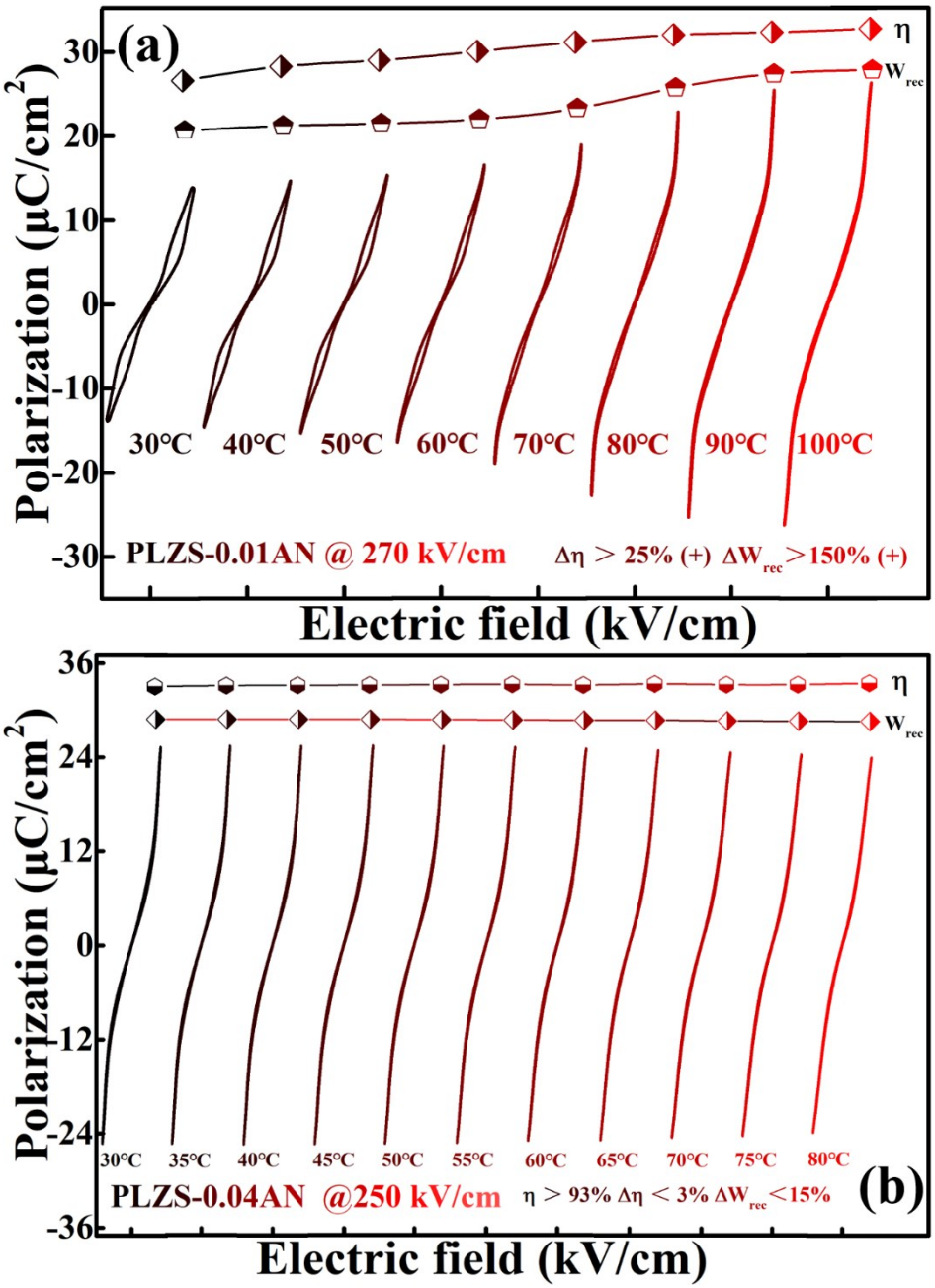

Figure S7 a)-b) The P-E loops as a functions of the rising temperatures under the electric field more than P_1 while less than P_2 for sample AN1 and AN4, respectively.

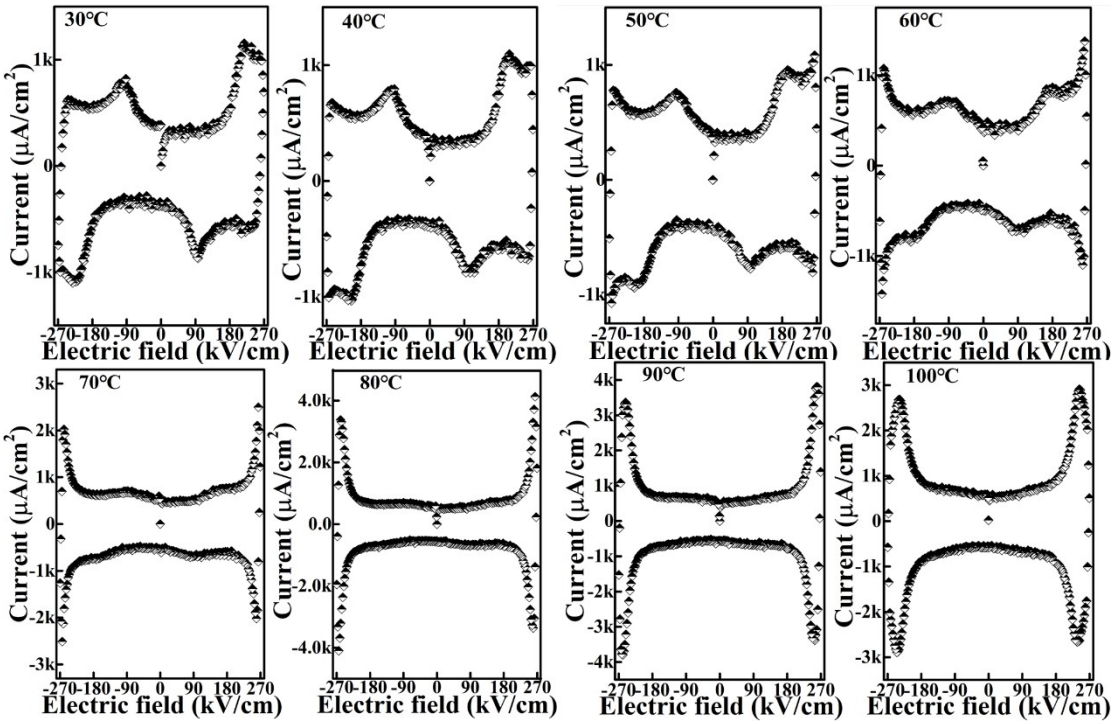

Figure S8 The Current-Electric field (J-E) curves at different temperatures under the above same electric field more than P_1 while less than P_2 for sample AN1.

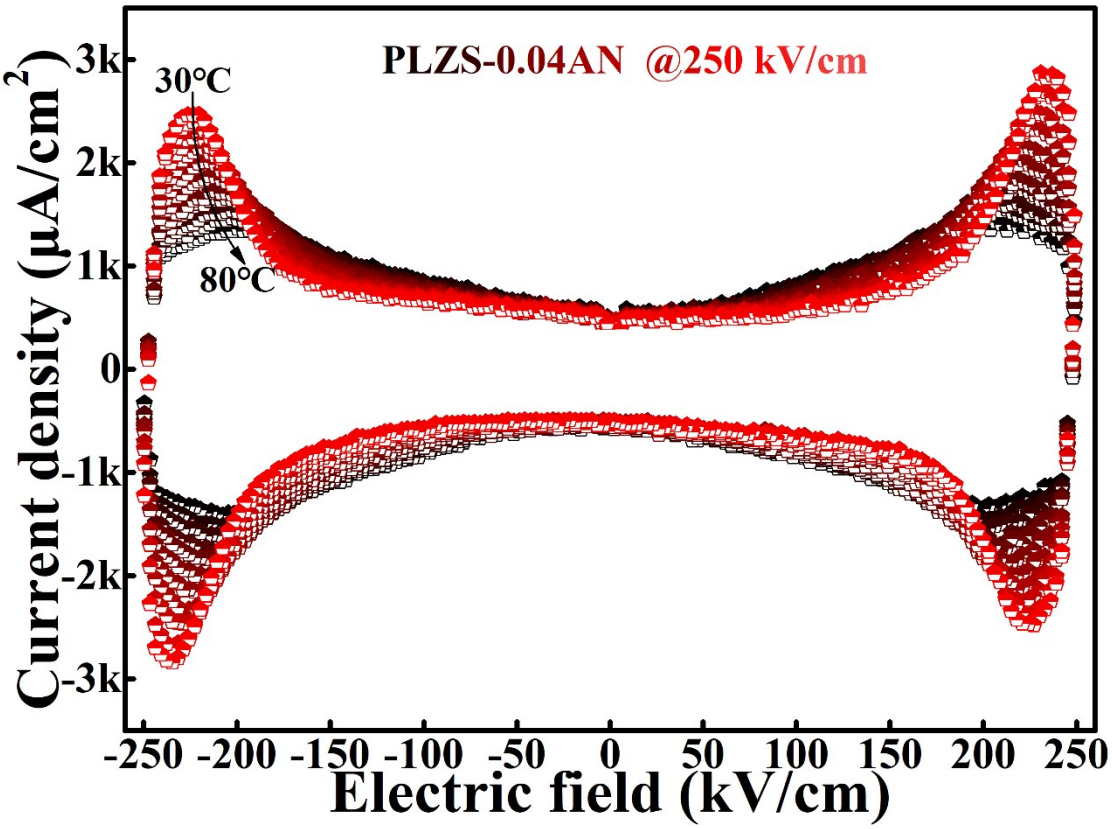

Figure S9 The J-E curves at different temperatures under the electric field more than the critical one for sample AN4.

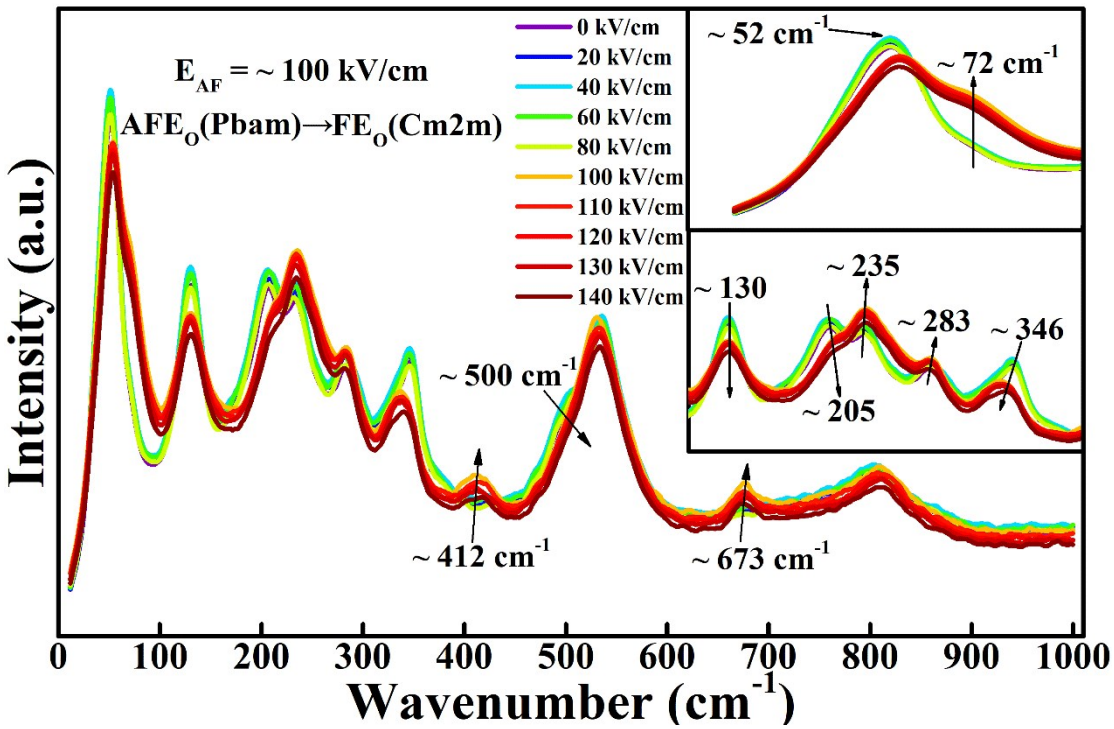

Figure S10 The Raman spectra ranging from 10 cm^{-1} to 1000 cm^{-1} as a function of the external electric field for some anonymous but pure isomorphous orthorhombic AFE with the same space group of Pbam compared with that of the $PbZrO_3$.

Experimental Section

Fabrications process of samples: The (1-x) $(Pb_{0.97}La_{0.02})(Zr_{0.6}Sn_{0.4})O_3$-x $AgNbO_3$ (x=0.01, 0.02, 0.03 and 0.04) antiferroelectric ceramics, abbreviated to AN1 to AN4 ("AN" refers to addition of $AgNbO_3$, the number refers to the ratio of addition), were prepared via the combination of traditional solid-state reaction and high energy ball milling. Dried raw materials of Pb_3O_4, La_2O_3, ZrO_2, SnO_2, Ag_2O, Nb_2O_5 with analytical purity, were weighed separately according to stoichiometry with a 2% molar ratio excess of Pb_3O_4 to compensate the loss of Pb during calcination. The oxide mixtures were then ball milled for 16h with ethanol and calcined for 3h at 900℃ to form the main crystal structure. High energy ball milling method was carried out to get refined powder size and elevated activity. Dozens of drops of PVA were added into crushed powders and then the mixture was pressed into green pellets with diameter of 10 mm. After burning out the PVA, the green pellets were kept at a high sintering temperature of 1300℃ for 3 hours. The lead atmosphere compensated with sheets consisting of equal molar of PbO and ZrO_2 in closed alumina crucible during sintering process is necessary and important. The obtained ceramics were then polished and coated with electrode for the electrical measurements.

P-E loops, dielectric properties measurements: Polarization–electric field hysteresis loops under frequency of 10 Hz were detected with ferroelectric test system (Premier II, Radiant Technologies Inc.) and the P-E loops under variable temperature were carried out with additional high-temperature probing stage. The LCR meter (Agilent E4980A, Santa Clara, CA) was adopted to get temperature-dependent dielectric properties under a temperature range of 20℃-500℃ in the frequency range of

1kHz-100kHz. By the way, all samples for P-E loops measurements are 0.1 mm in thickness and 2 mm in electrode diameter. As for dielectric measurement, samples with thickness of 0.4 mm and electrode diameter of 6 mm were applied.

Charge and discharge: The charge-discharge properties were investigated by a specially designed RLC load circuit with high-speed discharge resistance and inductance, the applied resistance is 950 Ω.

SEM: The free-surface microstructure observations were obtained using a field emission scanning electron microscope (SEM, EMP-800, Tokyo, Japan) and the samples were broken merely without extra process.

Room temperature phase structure: The samples of as-sintered were crushed into powders and then examined using X-ray diffractometer (XRD, D8 Advance, Bruker AXS GmbH, Germany) with scanning speed of 0.6°/min over the range of 20–80°. Raman spectra under different temperature for carefully polished samples were carried out using Horiba Lab-Ram HR800 spectrometer with green laser of 532nm accompanying with additional temperature probing stage.

Field-induced phase transition: XRD patterns under different temperatures were collected using X-ray diffractometer (PANalytical Empyrean, Holland). In-situ Raman spectra as a function of electric field at the selected temperature were carried out using the same spectrometer accompanying with additional heating and voltage adding devices. The samples for in-situ Raman observations with thickness of 0.1 mm and electrode diameter of 2 mm were specially processed with semitransparent gold electrode by DC sputtering.