Supplementary Information

Ultrahigh energy storage and electrocaloric performance achieved in $SrTiO_3$ amorphous thin films via polar clusters engineering

Supplementary Note 1: Energy storage characteristics of a dielectric

Generally, the discharging energy storage density (W) of dielectric capacitors can be estimated from the polarization versus electric filed (P-E) curves and calculated with the following equation:

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

where E is the applied electric field, P is the polarization， $P_{\max}$ is the maximum polarization and P_r is the remnant polarization. The energy conversion efficiency (η) can be expressed as:

$$\eta = \frac{W}{W + W_{loss}} \times 100\% \tag{2}$$

where W_{loss} is the energy storage loss. Considering the equations above, it is clear that the W of dielectric materials is determined by the $P_{\max}$, P_r and E, where E is limited by the dielectric breakdown strength (BDS). In addition, if dielectric materials can maintain smaller P_r and slim hysteresis loops at high electric field, high energy efficiency can be achieved.

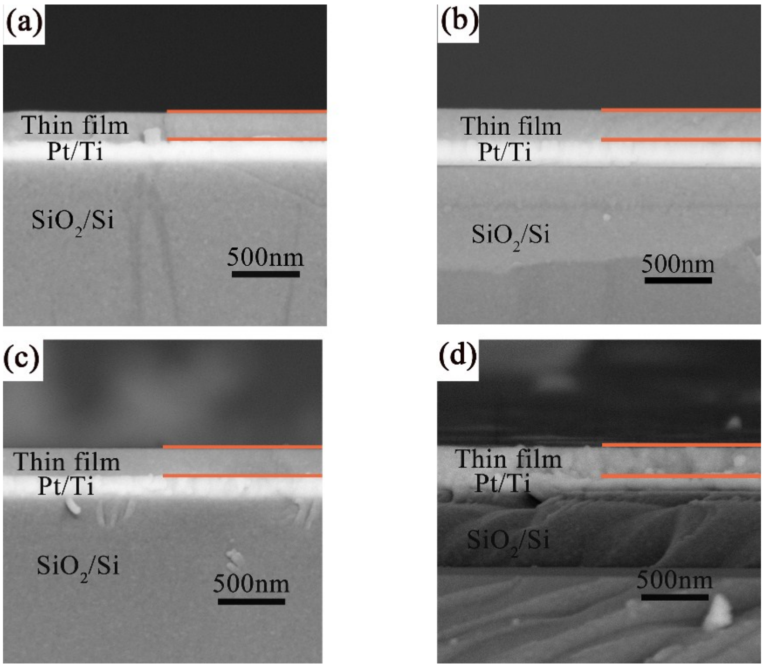

Fig. S1. The SEM images of $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}(Ti_{0.99}Mn_{0.01})O_3$ thin films with different annealing temperature (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 650 °C.

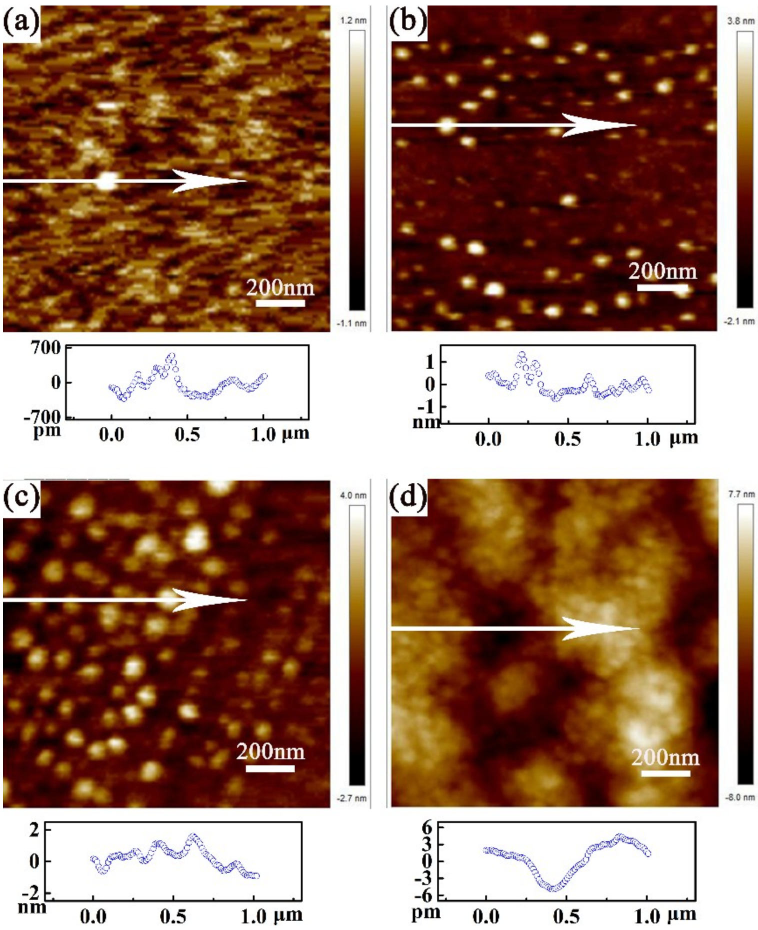

Fig. S2. The surface micrographs and the corresponding line scan profiles of $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}(Ti_{0.99}Mn_{0.01})O_3$ thin films with different annealing temperature (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 650 °C. The AFM profiling line is represented by the white arrow.

Supplementary Note 2: Breakdown strength

From the equation (1), it is evident that the energy storage density of dielectric capacitors is strongly related to its BDS. The BDS greatly affects the reliability and energy storage performance of dielectric capacitors. In order to obtain the full value of energy storage density, the Weibull distribution of BDS for $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}(Ti_{0.99}Mn_{0.01})O_3$ thin films annealed at different temperature is shown in Fig. S3. The Weibull distribution can be evaluated by the following equations:

$$X_i = \ln(E_i) \tag{3}$$

$$Y_i = \ln(- (\ln(1 - i/(n + 1)))) \tag{4}$$

where X_i and Y_i are two parameters in Weibull distribution function, i is the serial number of samples (i = 1,2,. . .) and n is the sum of specimens of each sample. E_i is the specific breakdown voltage of each specimen in the experiments and is arranged in ascending order of $E_1<E_2<E_3<...E_i<..E_n$.

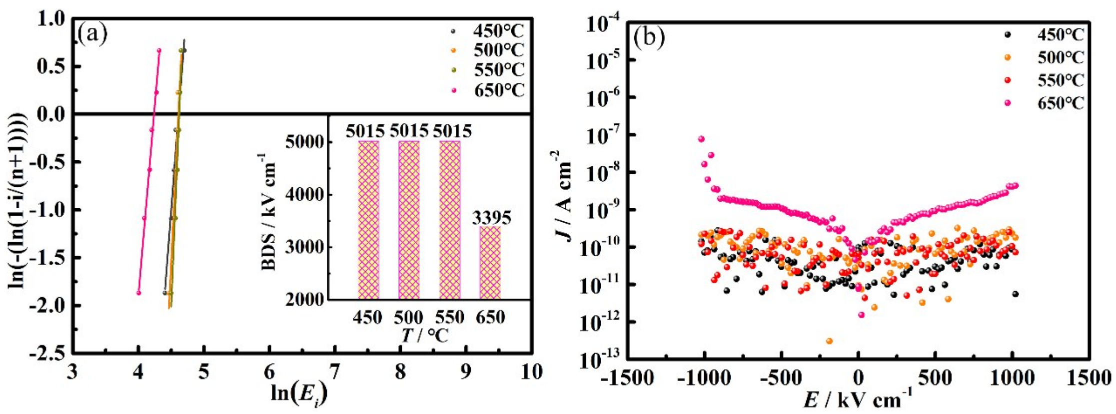

Fig. S3. a) Weibull distribution and fitting lines of BDS of $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}(Ti_{0.99}Mn_{0.01})O_3$ thin films with different annealing temperature. b) Leakage current characteristics of all samples.

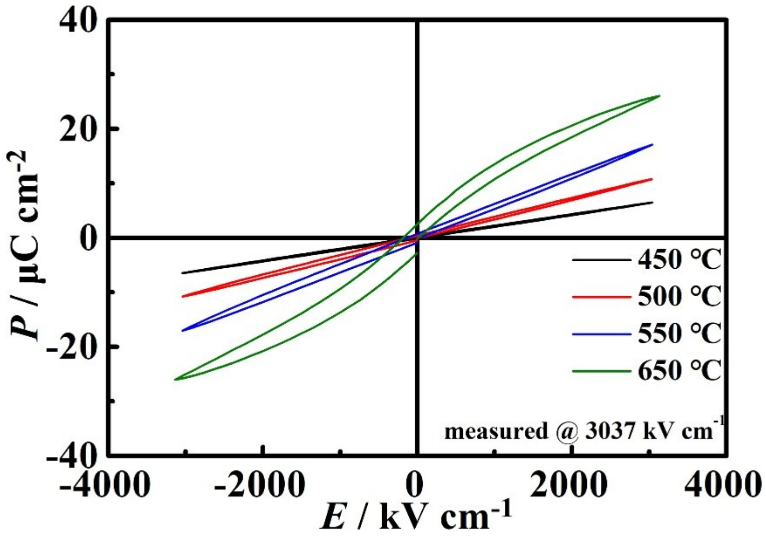

Fig. S4. *P-E* hysteresis loops of $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}(Ti_{0.99}Mn_{0.01})O_3$ thin films annealed at different annealed temperature.

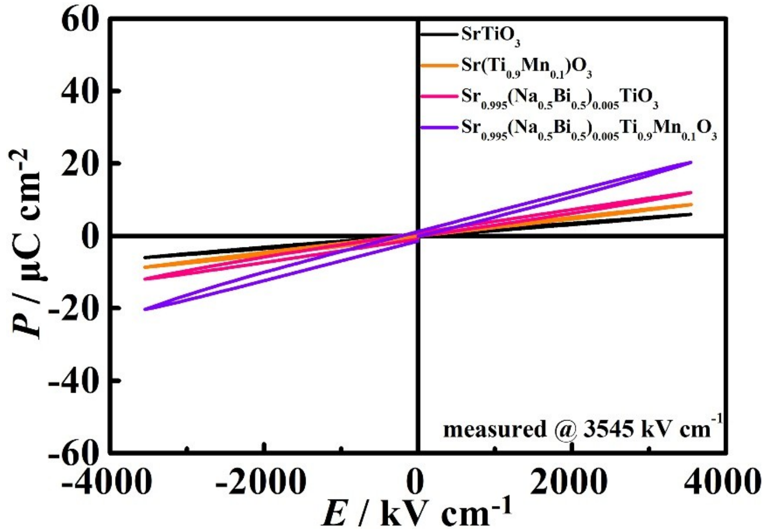

Fig. S5. *P-E* hysteresis loops of $SrTiO_3$, $SrTi_{0.99}Mn_{0.01}O_3$, $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}TiO_3$ and $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}(Ti_{0.99}Mn_{0.01})O_3$ thin films annealed at 550 °C.

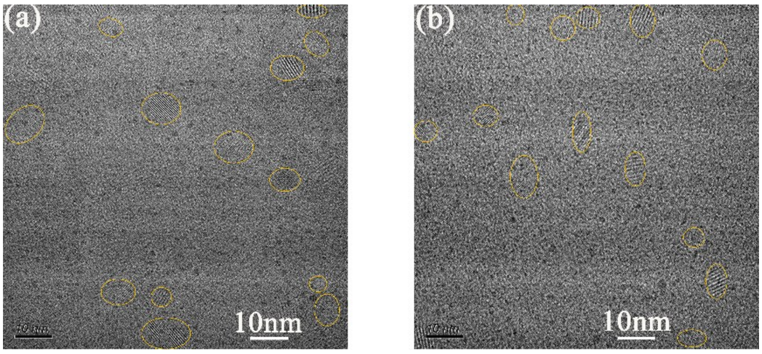

Fig. S6. High-magnification TEM images of the thin film annealed at 550 °C.

Supplementary Note 3: Arrhenius law

The activation energy of polar clusters can be calculated according to the Arrhenius law:

$$P(T) \propto \exp(-E_a/(k_B T)) \tag{5}$$

where E_a is the activation energy, T is the absolute temperature and k_B is the boltzmann constant. The E_a can be calculated from the plots of lnP versus 1/T.

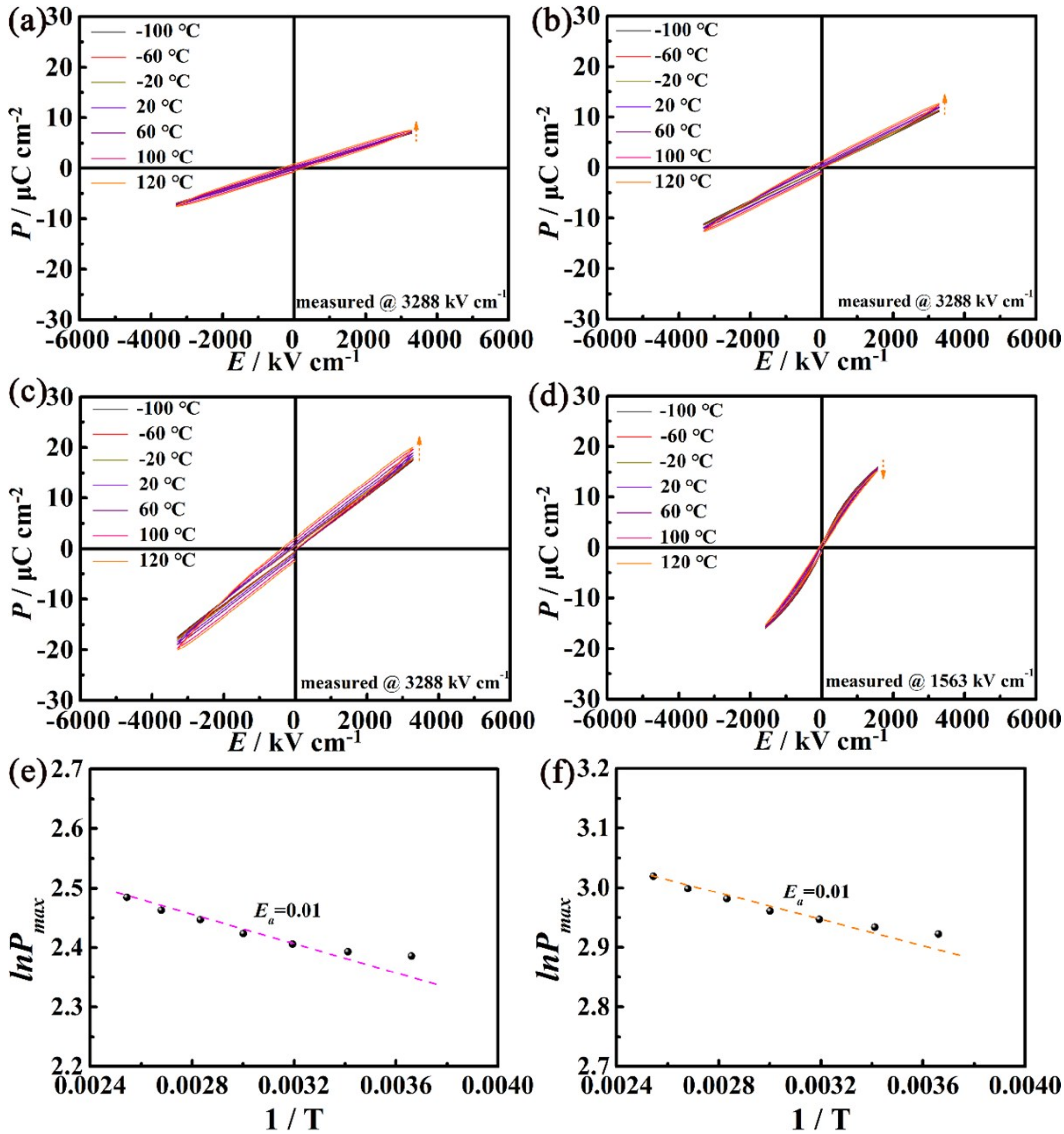

Fig. S7. a-d) Temperature dependent *P-E* loops of $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}(Ti_{0.99}Mn_{0.01})O_3$ thin films annealed at different temperature (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 650 °C. e-f) An Arrhenius plots of maximum polarization of thin films annealed at different temperature (e) 500°C and (f) 550 °C.

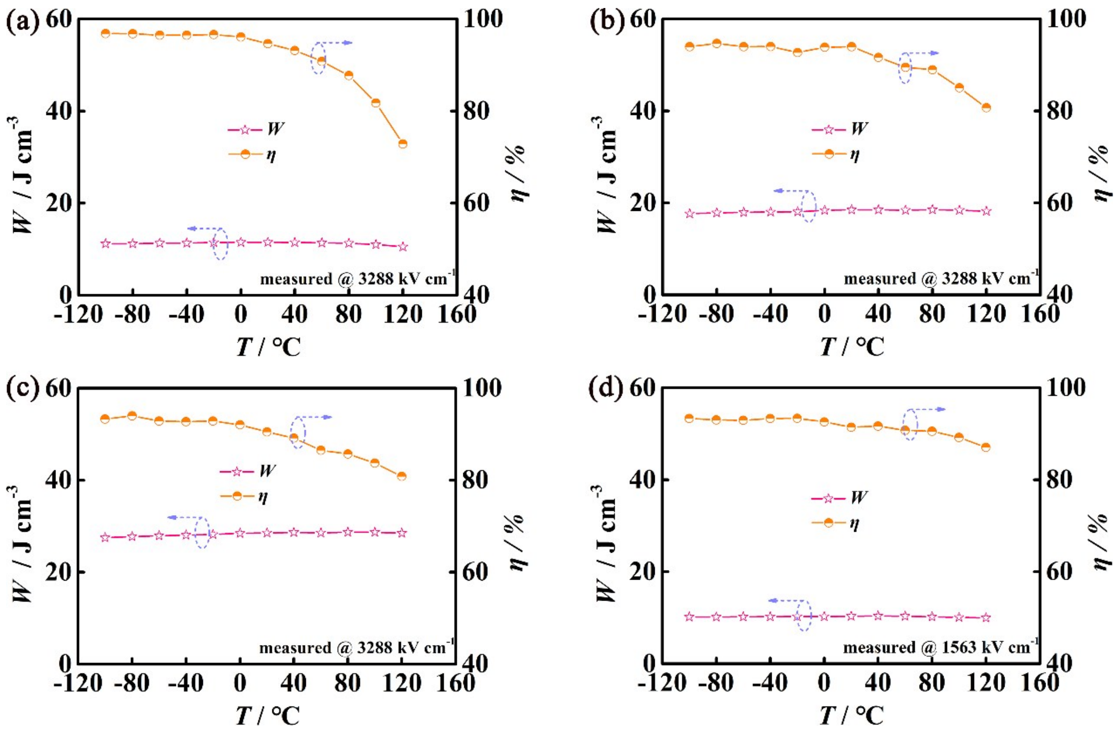

Fig. S8. The thermal stability of the recoverable energy storage density of $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}(Ti_{0.99}Mn_{0.01})O_3$ thin films annealed at different temperature (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 650 °C.

Supplementary Note 4: Electrocaloric effect of a dielectric

Based on Maxwell relationship $(\partial P/\partial T)_E=(\partial S/\partial E)_T$, reversible adiabatic changes in entropy ΔS and temperature ΔT of thin films can be expressed as follows:

$$\Delta S = -\frac{1}{\rho}\int_0^E \left(\frac{\partial P}{\partial T}\right)_E dE \quad (6)$$

$$\Delta T = -\frac{T}{\rho C_p}\int_0^E \left(\frac{\partial P}{\partial T}\right)_E dE \quad (7)$$

where T is the operation temperature, P is the maximum polarization at the applied electric field E, ρ is the density and C_p is the heat capacity that is assumed to be constant in the whole temperature range studied. The ρ and C_p in the temperature range studied are 5.13 g cm^{-3} and 0.542 J K^{-1} g^{-1}, respectively.

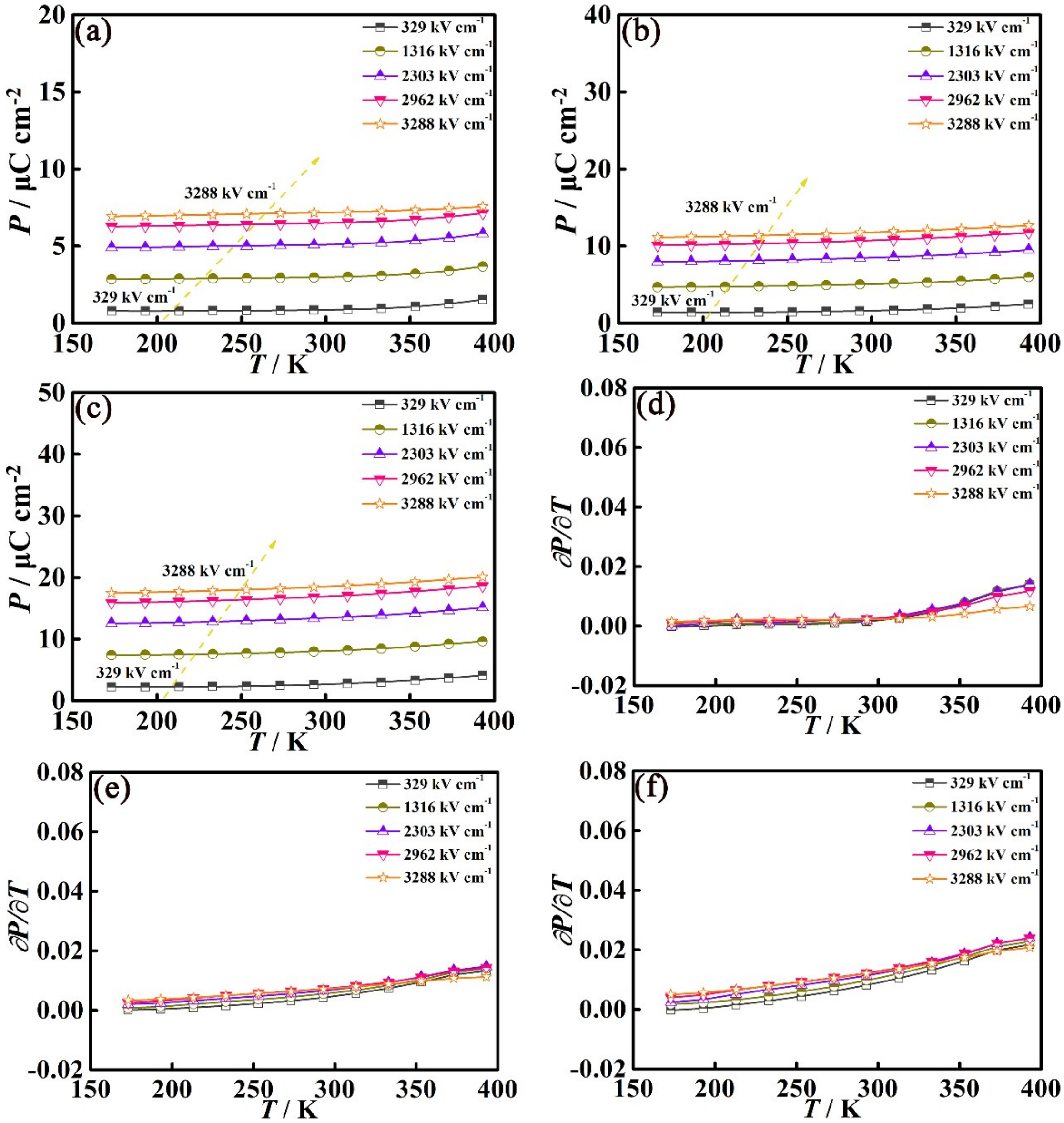

Fig. S9. a-c) Polarization-temperature plot of $Sr_{0.995}(Na_{0.5}Bi_{0.5})_{0.005}(Ti_{0.99}Mn_{0.01})O_3$ thin films annealed at different temperature (a) 450 °C, (b) 500 °C and (d) 550 °C. d-f) ∂P/∂T- temperature plot of thin films annealed at different temperature (d) 450 °C, (e) 500 °C and (f) 550 °C.