Supporting Information

Colossal Negative Electrocaloric Effects in Lead-free Bismuth Ferrite-based Bulk Ferroelectric Perovskite for Solid-state Refrigeration

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Experimental Section

The lead-free polycrystalline ceramics (1-x)$BiFeO_3$-x$BaTiO_3$ with x= 0.28, 0.30, 0.32 and 0.34 were fabricated via a conventional solid-state reaction. Bi_2O_3 (99.99%), Fe_2O_3 (99%), $BaCO_3$ (99%), TiO_2 (99.8%) powders were used as the raw materials. The mixed oxides were calcined at 800 ℃ for 5h and pressed into 13-mm-diameter pellets. $MnCO_3$ (0.15% wt) was added into the samples to increase the resistivity of BFO-based ceramics before calcination.[20] The pellets were buried in the calcined powders in closed crucibles and sintered at 1000 ~ 1020 ^oC for 3 hours with a heating rate of 5 ^oC /min. The phase composition of the samples was characterized using X-ray diffraction (XRD) (Rigaku RAX-10, Tokyo, Japan) at room temperature. The specific heat capacity of the ceramics was measured with a differential scanning calorimeter (DSC, Q2000). Silver films were painted on the surfaces of ceramic pellets as electrodes before electrical measurements. The dielectric constant was measured with an inductance, capacitance and reistance (LCR) meter. The electric field-polarization (P-E) hysteresis and current switching peak loops were measured using an aixACCT TF 2000 analyzer ferroelectric measuring system (aixACCT Co., Aachen, Germany). The leakage current measurements were also recorded by an aixACCT TF 2000 analyzer ferroelectric system. *In-situ* Transmission Electron Microscopy (TEM) were carried out on a JEM-2100F (Japan) operating at an acceleration voltage of 200kV. The bulk ceramics for TEM measurements were prepared by mechanical polishing, dimpling and ions milling until electron transparency. Bright field images and each corresponding selected area electron diffraction patterns were recoreded with a charge-coupled device camera.

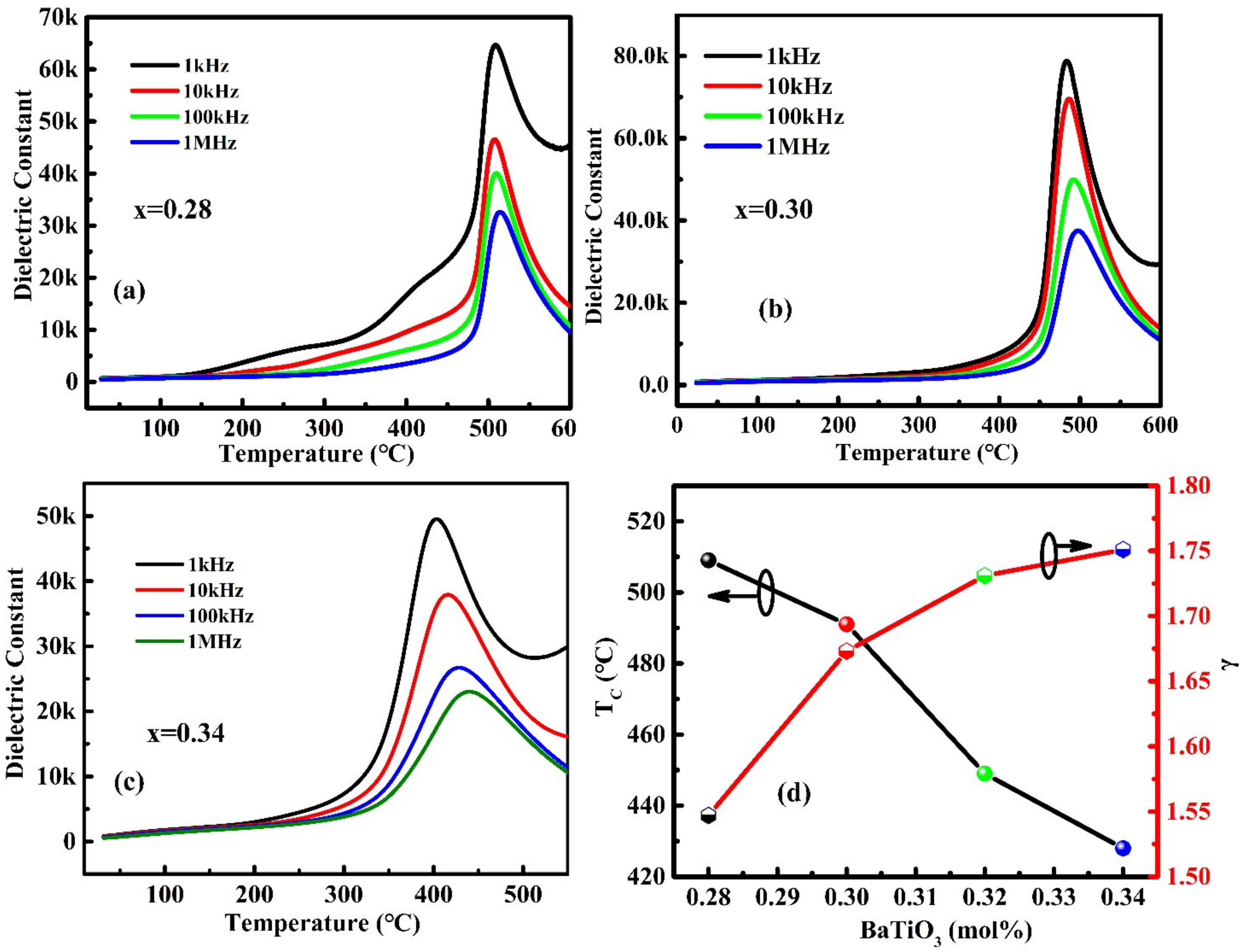

Figure S1 Dielectric constant as a function of temperature and frequency for (1-x)BFO-xBT bulk ceramics (a) x=0.28, (b) 0.30 and (c) 0.34. (d) The diffuseness parameter (γ) and Curie Temperature (Tc) for different composition (1-x)BFO-xBT ceramics (x=0.28,0.30,0.32,and 0.34)

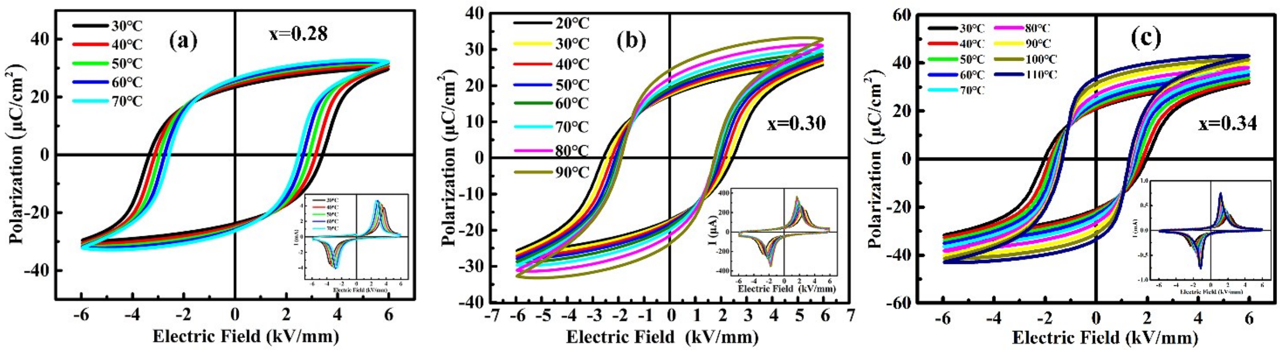

Figure S2 Temperature-dependent polarization-electric field hysteresis for (1-x)BFO-xBT (x=0.28,0.30,0.32,and 0.34) bulk ceramics. Note that the corresponding inset of (a), (b) and (c) shows the corresponding current switching peak-electric field loops under different temperature

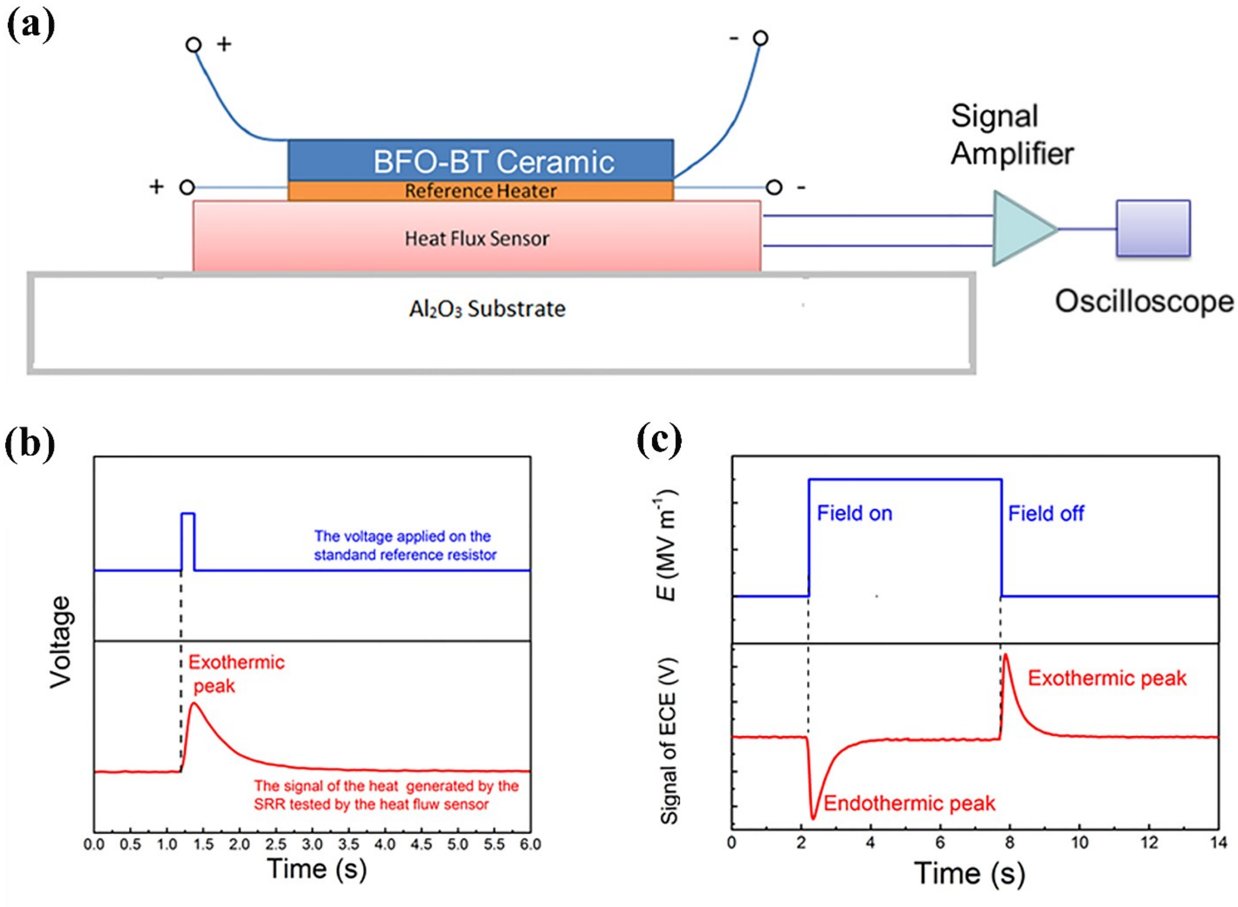

Figure S3 Schematic illustration of the EC effect measurement system. (b) and (c) shows the schematic isothermal heat flow curves under applied electric field excitations for the specimens.

Firstly, a voltage pulse V with a duration of t is applies on a standard reference resister heater R_{sr} (V is applied by the synthesized function generator, Stanford Research Systems DS345), to produce a heat $Q_h = (V^2/R_{sr})t$ collected by the heat flux sensor (RdF P/N 27134–3) and amplified by the low-noise preamplifier (Stanford research systems RS560), and eventually recorded by a oscilloscope (Fig. 3a and b). Subsequently, high electric fields were applied on the BFO-BT specimens to stimulate the ECE. By comparing the area of the endothermic peak (Fig. 3c) generated by the ECE cooling energy (Q_{ECE}) with the area of the exothermic peak generated by the heating energy of R_{sr}, the Q_{ECE} is obtained. Concurrently, ΔS and ΔT are obtained via $Q_{ECE}=vT\Delta S$ and $\Delta T=T\Delta S/C_p$ (v is the volume of the EC sample, T is the environmental temperature, and C_p is the specific heat of the EC material).

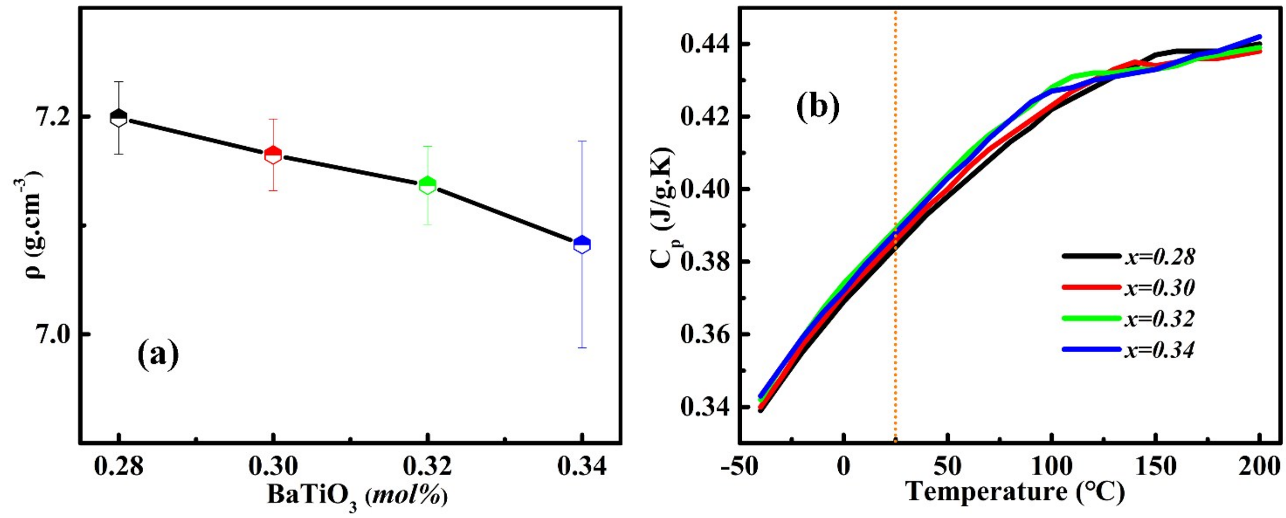

Figure S4 (a) The mass density measured by the Archimedes method and (b) The temperature-dependence of the heat capacity (C_P) for (1-x)BFO-xBT (x=0.28,0.30,0.32,and 0.34) bulk ceramics

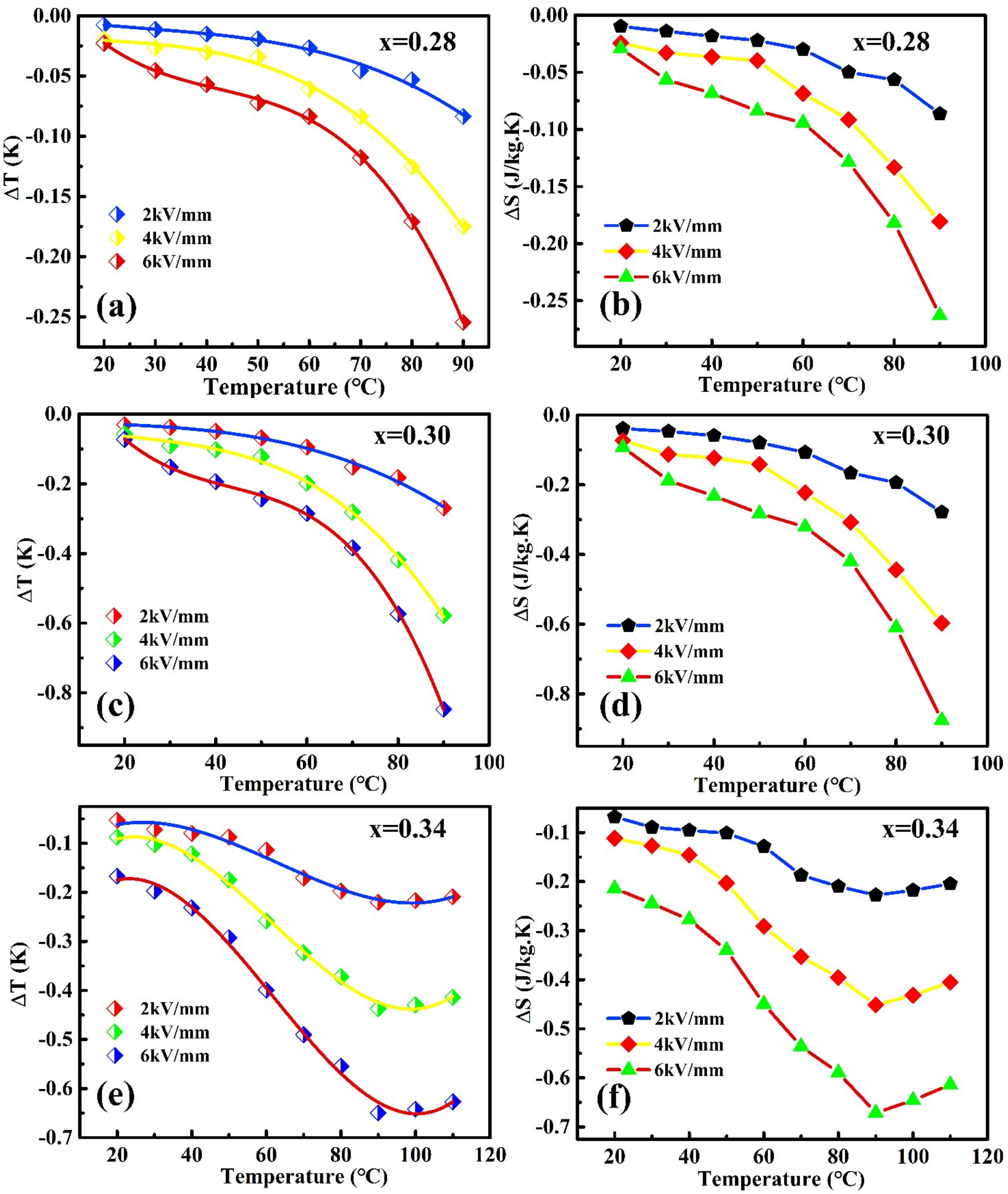

Figure S5 The changes in ΔT and ΔS of the (1-x)BFO-xBT bulk ceramics as a function of temperature (a)-(b) x = 0.28, (c)-(d) x = 0.30, (e)-(f) x = 0.34 Note that all ECE results are obtained from the heat flux sensor.

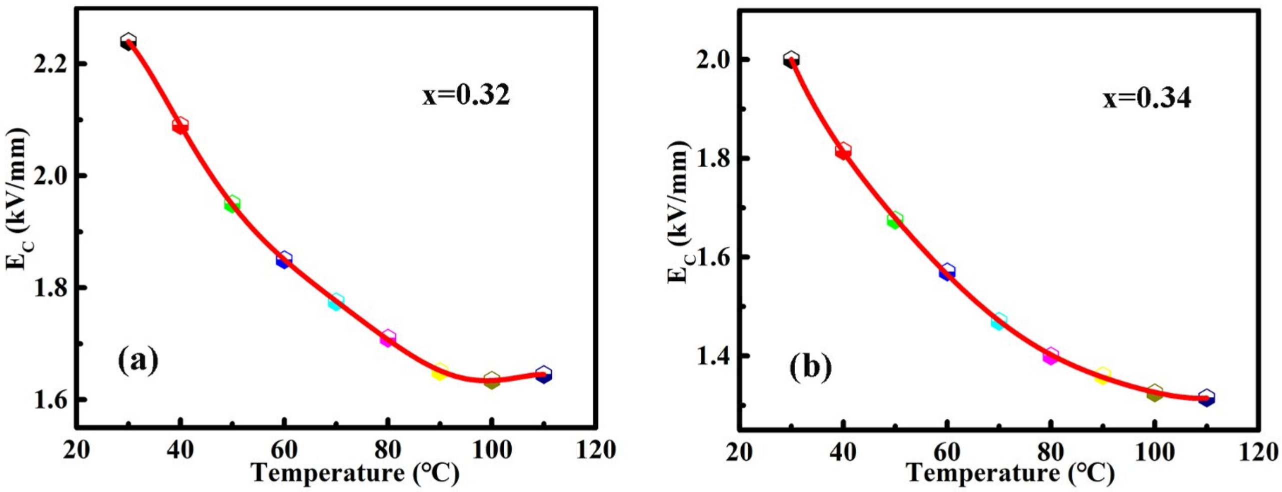

Figure S6 Temperature dependence of the coercive field (Ec) for (1-x)BFO-xBT ceramics (a) x = 0.32 (b) x = 0.34