Supplementary Information

The Large Electrocaloric Effect in Lead-free $Ba(Hf_xTi_{1-x})O_3$ Ferroelectric Ceramics for Clean Energy Applications

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EXPERIMENTAL SECTION

The BHT (x=0.03, 0.05, 0.08 and 0.11) ceramics synthesized by a solid-state process. Reagent-grade $BaCO_3$, TiO_2 and HfO_2 powders were batched stoichiometrically according to the nominal compositions BHT. Raw powders were ball milled in alcohol for 24 h and dried, followed by calcinations at 1100 ^oC for 2 h. The calcined powders were mixed with alcohol milling for 16 h and dried. After that, they were mixed thoroughly with a Polyvinyl butyral (PVB) binder solution and uniaxially pressed into discs of 12 mm in diameter pellet. These discs were sintered at 1450 ^oC for 5 h in air. Silver paste was painted on both surfaces of the disc samples and then fired at 650 ^oC to form the electrode.

The crystal structures of the sintered ceramics were characterized using X-ray diffraction (XRD, Rigaku ULTIMA-III). The surface microstructure of BHT ceramics were obtained by a scanning electron microscopy (SEM, S-3400N, Hitachi, Japan). Dielectric measurements were performed using a Agilent E4980A in the frequency range from 100 Hz to 1 MHz and in the temperature range from 25 to 600 ^oC with a heating rate of 3 ^oC/min. *P-E* loops were obtained by a ferroelectric test system (Premier II, Radiant Technology, USA).

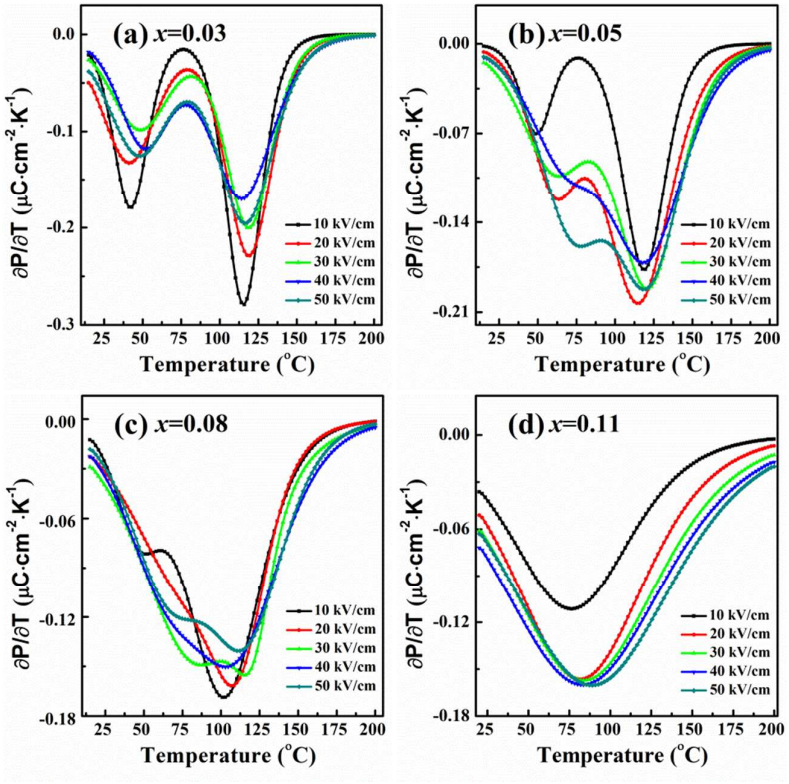

Figure S1. The pyroelectric coefficient $\partial P/\partial T$ as a function of temperature of BHT (a) $x = 0.03$, (b) $x = 0.05$, (c) $x = 0.08$, (d) $x = 0.11$ ceramics at various electric fields.

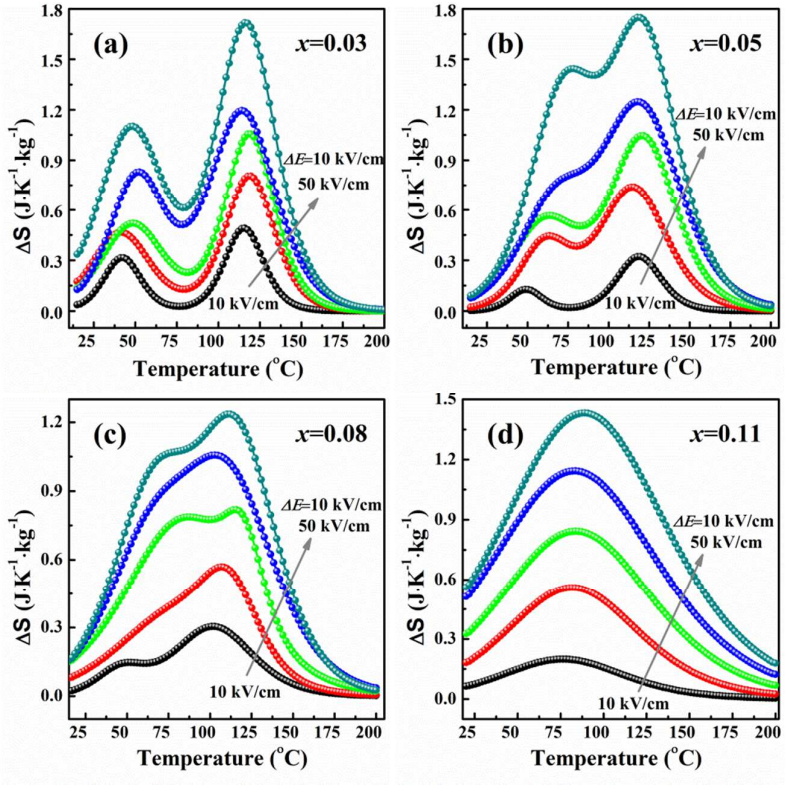

Figure S2. Isothermal entropy change ΔS as a function of temperature of BHT (a) x = 0.03, (b) x = 0.05, (c) x = 0.08, (d) x = 0.11 ceramics at various electric fields.