Electronic Supplementary Information

Electro-caloric effect in BCZT single crystal

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Table S1 Atomic percent of Ba, Ca, Zr, and Ti in three different parts of as-grown BCZT single crystal

	Ba	Ca	Zr	Ti
Part 1	81.9%	18.1%	99.4%	0.6%
Part 2	78.9%	21.1%	99.4%	0.6%
Part 3	75.0%	25.0%	99.3%	0.7%

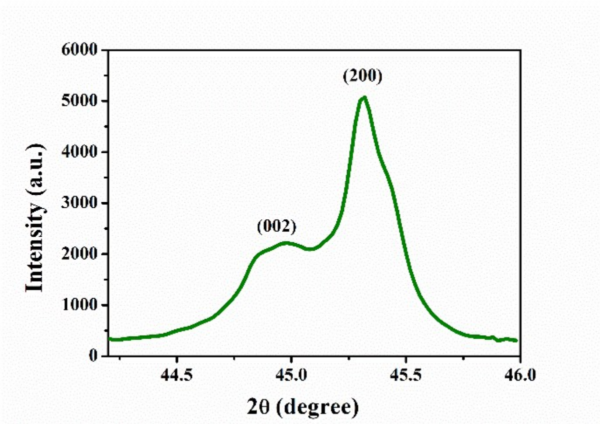

Fig. S1 Enlarged powder XRD of the as-grown BCZT single crystal around 45°.

The formula derivation of Eq. (4):

Eq. (4) in the main text was deduced from the thermodynamic relations between temperature and entropy.[1,2] The entropy can be written as a sum of two parts:

$$S(E,T) = S_{dip}(E,T) + S_{ph}(E,T) \tag{S1}$$

The first part can be written as a function of the polarization, while the second part is a field independent contribution of phonons, electrons and so on. In an ECE process (adiabatic), the total change of entropy $\Delta S(E,T)$ is zero. We can obtain Eq. (S2):

$$S_{ph}(T_2) - S_{ph}(T_1) = -\,[S_{dip}(E_2,T_2) - S_{dip}(E_1,T_1)] \tag{S2}$$

The change of lattice entropy is as follow:

$$S_{ph}(T_2) - S_{ph}(T_1) = \int_{T_1}^{T_2} \frac{C_{ph}(T)}{T} dT \tag{S3}$$

For most of the ECE materials, the temperature change dT is small, thus Eq. (S3) can be written as follow:

$$S_{ph}(T_2) - S_{ph}(T_1) = C_{ph}(T_1)\ln\frac{T_2}{T_1} \tag{S4}$$

Thus, $S_{dip}(E_1,T_1) - S_{dip}(E_2,T_2) = C_{ph}(T_1) ln\frac{T_2}{T_1}$,

So, $T_2 = T_1 exp\{\frac{1}{C}(S_1 - S_2)\}$, where C is $C_{ph}(T_1)$, S_1 is $S_{dip}(E_1,T_1)$, S_2 is $S_{dip}(E_2,T_2)$, which agrees with Eq. (4) in the main text. The Eq. (4) indicates the relationship between the temperature change (T_2-T_1) and the polarization induced entropy. From this equation, when the entropy increases ($S_2>S_1$, $\exp\left\{\frac{1}{C}(S_1 - S_2)\right\} < 1$), the temperature decreases ($T_2<T_1$), corresponding to a negative temperature change. In the temperature range of -60 ^{o}C to 5 ^{o}C, when the electric field is applied along [001], the BCZT crystal is in 4O state. In this case, the polarization aligns along [001], which causes a multiplicity of polarization orientation (more disordered) and an increase of S_{dip}. The increase of entropy leads to a temperature decrease, as shown above, corresponding to a negative ECE.

References

1. R. Pirc, Z. Kutnjak, R. Blinc, and Q. M. Zhang, *J. Appl. Phys.*, 2011, **110**, 074113.
2. N. Novak, Z. Kutnjak, and R. Pirc, *EPL*, 2013, **103**, 47001.