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

<table>
<thead>
<tr>
<th></th>
<th>Ba</th>
<th>Ca</th>
<th>Zr</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part 1</td>
<td>81.9%</td>
<td>18.1%</td>
<td>99.4%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Part 2</td>
<td>78.9%</td>
<td>21.1%</td>
<td>99.4%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Part 3</td>
<td>75.0%</td>
<td>25.0%</td>
<td>99.3%</td>
<td>0.7%</td>
</tr>
</tbody>
</table>

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.\textsuperscript{1,2} The entropy can be written as a sum of two parts:

\[ S(E,T) = S_{dip}(E,T) + S_{ph}(E,T) \]  

(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):

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

(S2)

The change of lattice entropy is as follow:

\[ S_{ph}(T_2) - S_{ph}(T_1) = \frac{1}{T_1} \int_{T_1}^{T_2} C_{ph}(T) \, dT \]  

(S3)

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

\[ S_{ph}(T_2) - S_{ph}(T_1) = C_{ph}(T_1) \ln \frac{T_2}{T_1} \]  

(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,

\[ T_2 = T_1 \exp\left\{ \frac{1}{C} (S_1 - S_2) \right\}, \]

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 \( (S_2>S_1) \), the temperature decreases \( (T_2<T_1) \), corresponding to a negative temperature change. In the temperature range of -60 °C to 5 °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