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Inverse barocaloric effects in ferroelectric BaTiO$_3$ ceramics

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We use calorimetry to identify pressure-driven isothermal entropy changes in ceramic samples of the prototypical ferroelectric BaTiO$_3$. Near the structural phase transitions at $\sim$400 K (cubic-tetragonal) and $\sim$280 K (tetragonal-orthorhombic), the inverse barocaloric response differs in sign and magnitude from the corresponding conventional electrocaloric response. The differences in sign arise due to the decrease in unit-cell volume on heating through the transitions, whereas the differences in magnitude arise due to the large volumetric thermal expansion on either side of the transitions. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4961598]
Here we use temperature-dependent x-ray diffraction, and pressure-dependent calorimetry, to experimentally demonstrate BC effects in ceramics of the prototypical ferroelectric BTO. The combination of these two techniques is essential for evaluating contributions to the BC response that arise from the non-isochoric phase transitions and the volumetric thermal expansion on either side of each transition.26 At high temperatures, BTO displays a centrosymmetric cubic ABO$_3$ perovskite structure, with A cations at the corners, B cations at the centres, and oxygen anions at the face-centred positions. Near the transition between cubic (C) and tetragonal (T) phases, at Curie temperature $T_C \sim 400$ K, we find inverse isothermal entropy changes of magnitude $|\Delta S| \sim 1.6$ J K$^{-1}$ kg$^{-1}$ due to small changes of applied pressure $|\Delta p| \sim 1$ kbar (assuming ambient pressure to be zero, such that $|\Delta p| \sim p$). At lower temperatures, near the $\sim 280$ K transition between T and orthorhombic (O) phases, we find inverse isothermal entropy changes of magnitude $|\Delta S| \sim 1.3$ J K$^{-1}$ kg$^{-1}$, also with $|\Delta p| \sim 1$ kbar. We did not explore the $\sim 200$ K transition between O and rhombohedral (R) phases, as the change in unit-cell volume is small [Figure S1 of the supplementary material].

Powdered BTO (≥99.99%) from Sigma-Aldrich had a typical grain size of <1 μm. The powder was first cold-pressed isostatically in air at 10 kbar and then sintered in air at 1673 K for 48 h. The sintered ceramic (2.3 cm in diameter, 0.2 cm in thickness) was cooled down to room temperature at $\sim -3$ K min$^{-1}$. A small piece (~0.005 cm$^3$) was cut in order to perform temperature-dependent calorimetry and x-ray diffraction at ambient pressure. The larger remaining piece was used for pressure-dependent calorimetry.

Measurements of $\frac{dQ}{dT}$ at atmospheric pressure were performed using a commercial TA Q2000 differential scanning calorimeter at ±2 K min$^{-1}$ ($Q$ is heat, $T$ is temperature). Heat $Q_0$ was gathered and entropy change $\Delta S_0$ calculated across the first-order transitions were obtained after subtracting baseline backgrounds, with $T_1$ chosen above (below) each transition on cooling (heating), and $T_2$ chosen below (above) each transition on cooling (heating). The entropy change on partially driving each transition by heating to temperature $T$, with respect to each low-temperature phase, is $\Delta S(T) = \int_{T_1}^{T} (\frac{dQ}{dT'})/T' dT'$. The entropy change on partially driving each transition by cooling to temperature $T$, with respect to each low-temperature phase, is $\Delta S(T) = |\Delta S_0| - \int_{T_2}^{T} (\frac{dQ}{dT'})/T' dT'$.

High-resolution x-ray diffraction was performed in transmission-mode using Cu Kα$_1$ = 1.5406 Å radiation in an INEL diffractometer, with a curved position-sensitive detector (CPS120), and Debye-Scherrer geometry. The sample was introduced into a 0.3-mm diameter Lindemann capillary to minimise absorption, and temperature was varied using a liquid-nitrogen 700 series Oxford Cryostream Cooler. Lattice parameters were determined by pattern matching using FullProf software.

Measurements of $\frac{dQ}{dT}$ under hydrostatic pressure were performed at approximately ±2 K min$^{-1}$, using a differential thermal analyser constructed in-house. At high temperatures, we used an Irimo Bridgman pressure cell that operates at up to 3 kbar and a resistive heater (room temperature-473 K). At low temperatures, we used a Cu-Be Bridgman pressure cell that operates at up to 3 kbar and a circulating thermal bath (Lauda Proline RP 1290, 183-473 K). In order to guarantee optimal thermal contact between the heat sensor and the sample, a chromel-alumel thermocouple was inserted inside a hole that was drilled in the centre of the large BTO ceramic sample. The ceramic sample and thermocouple were then immersed in the pressure-transmitting medium (Caldic silicon oil for high-temperature measurements; DW-Therm, Huber Kältemaschinenbau GmbH for low-temperature measurements).

The first-order structural phase transitions are seen in calorimetry [Figure 1(a)] to be sharp, with a small thermal hysteresis of ~4 K (C-T) and ~7 K (T-O). Integration of $\frac{dQ}{dT}$ yields the thermally driven entropy change $\Delta S(T)$ [Figure 1(b)], with $|\Delta S_0| = 2.4 \pm 0.2$ J K$^{-1}$ kg$^{-1}$ for the full C-T transition and $|\Delta S_0| = 2.0 \pm 0.2$ J K$^{-1}$ kg$^{-1}$ for the full T-O transition. Integration of $\frac{dQ}{dP}$ across the full transition yields heats of $Q_0 = 960 \pm 90$ J kg$^{-1}$ (C-T) and $Q_0 = 560 \pm 60$ J kg$^{-1}$ (T-O). These values are in good agreement with previous experimental values$^{23,31}$ of $|\Delta S_0| \sim 2.4$ J K$^{-1}$ kg$^{-1}$ and $Q_0 \sim 900$ J kg$^{-1}$ for the C-T transition and are similar to previous values$^{31,32}$ of $|\Delta S_0| \sim 1.6$-2.3 J K$^{-1}$ kg$^{-1}$ and $Q_0 \sim 450$-640 J kg$^{-1}$ for the T-O transition.
On heating through the two transitions, x-ray diffraction data [Figure 1(c)] confirm the expected changes in crystal structure.\textsuperscript{22,23} The unit-cell volume \( V \) decreases sharply by \(-0.03\%\) (O-T transition, \( \Delta V_0 = -0.02 \pm 0.01 \text{ Å}^3 \)) and \(-0.11\%\) (T-C, \( \Delta V_0 = -0.07 \pm 0.02 \text{ Å}^3 \)). On either side of each transition, the volume thermal expansion is large [Figure S1 of the supplementary material], implying large additional BC effects.\textsuperscript{22,23} By writing isothermal BC entropy change per unit mass \( m \) due to pressure change \( \Delta p = p_2 - p_1 \) as\textsuperscript{4,28} \( \Delta S(p_1 \rightarrow p_2) = -m^{-1} \int_{p_1}^{p_2} (\partial V/\partial T)_p dp' \) (using the Maxwell relation \( m^{-1}(\partial V/\partial T)_p = -(\partial S/\partial p)_T \)), we therefore anticipate inverse BC effects in the transition regimes where \((\partial V/\partial T)_p = 0\), and conventional BC effects outside the transition regimes where \((\partial V/\partial T)_p > 0\).

\( dQ/dT \) measurements through the two transitions under various applied pressures are shown in Figure 2. For the C-T transition, there is a strong pressure-induced shift of transition temperature \( T_0 \), with \( dT_0/dp = -5.8 \pm 0.1 \text{ K kbar}^{-1} \) on heating and \( dT_0/dp = -5.4 \pm 0.2 \text{ K kbar}^{-1} \) on cooling [Figures 2(a) and 2(c)]. A larger shift of \(-7.9 \pm 2.0 \text{ K kbar}^{-1} \) on heating is obtained via the Clausius-Clapeyron equation \( dT_0/dp = \Delta V_0/\Delta S_0 \), using \( \Delta S_0 = 2.4 \pm 0.2 \text{ J K}^{-1} \text{ kg}^{-1} \) [Figure 1(b)] and specific volume change \( \Delta V_0 = -(0.19 \pm 0.03) \times 10^{-6} \text{ m}^3 \text{ kg}^{-1} \) [from Figure 1(c)]. These values of \( dT_0/dp \) are similar to those reported for BTO in the form of single crystals (\( \sim 4-6 \text{ K kbar}^{-1} \), Refs. 33–40) and ceramics (\( \sim 4-5 \text{ K kbar}^{-1} \), Refs. 36, 40, and 41), and they imply that the narrow first-order transition of width \( \sim 4 \text{ K} \) may be fully driven using low values of \( |\Delta p| \sim 1 \text{ kbar} \).

For the T-O transition, the pressure-induced shift in \( T_0 \) is weaker, with \( dT_0/dp = -3.5 \pm 0.1 \text{ K kbar}^{-1} \) on heating and \( dT_0/dp = -2.6 \pm 0.1 \text{ K kbar}^{-1} \) on cooling [Figures 2(b) and 2(c)]. A similar shift of \( dT_0/dp = -2.8 \pm 1.3 \text{ K kbar}^{-1} \) on heating is obtained via the Clausius-Clapeyron equation, using \( \Delta S_0 = 2.0 \pm 0.2 \text{ J K}^{-1} \text{ kg}^{-1} \) [Figure 1(b)] and specific volume change \( \Delta V_0 = -(0.06 \pm 0.03) \times 10^{-6} \text{ m}^3 \text{ kg}^{-1} \) [from Figure 1(c)]. These values of \( dT_0/dp \) are similar to those reported for single-crystal BTO (\( \sim 3 \text{ K kbar}^{-1} \), Refs. 35, 37, 40, and 42) and indicate that the wider first-order transition of width \( \sim 7 \text{ K} \) may be fully driven using \( |\Delta p| \sim 2 \text{ kbar} \).

For each of the two transitions, integration of \((dQ/dT)/T\) at finite pressure reveals that the entropy change \(|\Delta S_0|\) decreases with increasing pressure [Figure 2(d)]. This fall in \(|\Delta S_0|\) arises because of...
Additional changes in isothermal entropy \( \Delta S_s(p) \) that are conventional, reversible, and opposite in sign with respect to the pressure-driven isothermal entropy changes associated with each transition. These additional changes in entropy are challenging to detect via the calorimetry used for Figure 2 but may be expressed away from the first-order transitions via

\[
\Delta S_s(p) = -\left[ m^{-1} \partial V/\partial T \right]_{p=0} \Delta p,
\]

where we have used the aforementioned Maxwell relation with \( S_s \) replacing \( S \) and with \( \partial V/\partial T \) assumed independent of pressure.\(^{3,28}\)

In order to plot \( \Delta S(T, p) \) with respect to the zero-pressure entropy at a temperature \( T_\star \) above the C-T transition [Figures 3(a) and 3(b)] and the T-O transition [Figures 4(a) and 4(b)], we obtained finite-pressure plots of \( \Delta S(T) \) [from the integration of data in Figures 2(a) and 2(b)] that we displaced\(^{28}\) at \( T_\star \) by evaluating \( \Delta S_s(p) \) at this temperature. Note that \( \Delta S_s(p) \) was evaluated at \( T_\star > T_0(p) \) to avoid the forbidden possibility of \( T_0(p) \) falling to \( T_\star \) at high pressure.

For the C-T transition, our plots in Figure 3(a) of \( \Delta S(T, p) \) for \( \partial Q/\partial T \) data obtained on heating permit us to establish isothermal BC effects on applying pressure [Figure 3(c)], as heating and high pressure both favour the high-temperature cubic phase with smaller volume. Similarly, our plots in Figure 3(b) of \( \Delta S(T, p) \) for \( \partial Q/\partial T \) data obtained on cooling permit us to establish isothermal BC effects on decreasing pressure [Figure 3(d)], as cooling and low pressure both tend to favour the low-temperature tetragonal phase with larger volume. Values of \( |\Delta S(T, p)| \) on applying and removing pressure are similar at all temperatures studied. The BC response near the C-T transition is therefore highly reversible, consistent with the low thermal hysteresis of the transition [Figures 1(a) and 1(b)]. The peak isothermal entropy change \( |\Delta S| \sim 1.6 \pm 0.2 \text{ J K}^{-1} \text{ kg}^{-1} \) near \( \sim 400 \text{ K} \) is achieved with a low value of \( |\Delta p| = 1 \text{ kbar} \) [Figures 3(c) and 3(d)], yielding large BC strengths,\(^3\) \( |\Delta S|/|\Delta p| \) and \( |Q|/|\Delta p| \) (Table I). Larger pressures extend inverse reversible BC effects to lower temperatures, causing an increase of refrigerant capacity RC [Figure 5(b)], despite the reduction in \( |\Delta S(p)| \) [Figure 2(d)] and thus the peak value of \( |\Delta S(p)| \) [Figure 5(a)]. Note that recently predicted BC effects \((|\Delta S| \sim 3.9 \text{ J K}^{-1} \text{ kg}^{-1} \text{ with 10 kbar at 353 K})\) are larger because additional entropy changes were neglected.\(^{37}\)
FIG. 3. Inverse barocaloric effects in BTO near the C-T phase transition. For (a) heating and (b) cooling, we show entropy change $\Delta S(T, p)$ with respect to $S(T = 375\,\text{K}, p = 0)$ (black dot), offsetting $\Delta S(T)$ at each pressure using additional entropy change $\Delta S_i(p)$ at $T_i = 410\,\text{K}$. Hence isothermal entropy change $\Delta S(p)$ for (c) increasing pressure ($0 \rightarrow p$) as deduced from (a), and (d) decreasing pressure ($p \rightarrow 0$) as deduced from (b). In each panel, the given pressure values increase as indicated by the horizontal arrow.

FIG. 4. Inverse barocaloric effects in BTO near the T-O phase transition. For (a) heating and (b) cooling, we show entropy change $\Delta S(T, p)$ with respect to $S(T = 260\,\text{K}, p = 0)$ (black dot), offsetting $\Delta S(T)$ at each pressure using additional entropy change $\Delta S_i(p)$ at $T_i = 292\,\text{K}$ for (a), and at $T_i = 282\,\text{K}$ for (b). Hence isothermal entropy change $\Delta S(p)$ for (c) increasing pressure ($0 \rightarrow p$) as deduced from (a), and (d) decreasing pressure ($p \rightarrow 0$) as deduced from (b). In each panel, the given pressure values increase as indicated by the horizontal arrow.
TABLE I. Comparison of inverse barocaloric effects and conventional electrocaloric effects in BTO. Isothermal entropy change $\Delta S$ and isothermal heat $Q$, at starting temperature $T$, due to changes of hydrostatic pressure $\Delta p$, and changes of electric field $\Delta E$. The corresponding strengths are $|\Delta S|/|\Delta p| = 1.6$ J K$^{-1}$ kg$^{-1}$ kbar$^{-1}$ and $|Q|/|\Delta p| = 660$ J kg$^{-1}$ kbar$^{-1}$ for the C-T transition, and $|\Delta S|/|\Delta p| = 1.3$ J K$^{-1}$ kg$^{-1}$ kbar$^{-1}$ and $|Q|/|\Delta p| = 365$ J kg$^{-1}$ kbar$^{-1}$ for the T-O transition. For $\Delta S$ and $Q$, bold entries denote data derived from direct measurements, other entries denote data derived from quasi-direct measurements. For all entries, $Q = T \Delta S$.

| Transition | $T$ (K) | Caloric effect | Single crystal or Polycrystal | $\Delta S$ (J K$^{-1}$ kg$^{-1}$) | $Q$ (J kg$^{-1}$) | $\Delta p$ or $\Delta E$ | References |
|------------|---------|----------------|-----------------------------|-----------------|-----------------|-----------------|------------|
| C-T        | 400     | BC Polycrystal | -2.1                        | 660             | 1 kbar          | This work       | 12         |
|            |         | EC Single crystal | 1.6                         |                 |                 |                 |            |
| T-O        | 280     | BC Polycrystal | $-2.3$                      | $-645$          | 1 kbar          | This work       | 43         |
|            |         | EC Single crystal | $-2.1$                      | $-840$          | 10 kV cm$^{-1}$ |                 |            |

For the T-O transition, our plots in Figures 4(a) and 4(b) of $\Delta S(T,p)$ for d$Q$/dT data obtained on heating and cooling permit us to establish isothermal BC effects on increasing pressure [Figure 4(c)] and decreasing pressure [Figure 4(d)]. Although the peak entropy change of $|\Delta S| \sim 1.3 \pm 0.2$ J K$^{-1}$ kg$^{-1}$ appears to be similar for $\Delta p = \pm 1$ kbar, the peak occurs at different temperatures, evidencing irreversible BC effects. This irreversibility, which is also seen for conventional EC effects near the T-O transition, arises because of the relatively large thermal hysteresis. Therefore caloric effects near the T-O transition are unsuitable for continuous cooling, and so we do not present RC values.

In summary, we have combined temperature-dependent x-ray diffraction data with pressure-dependent calorimetry to demonstrate BC effects in BTO ceramic samples. For the T-O phase transition at $\sim 280$ K, we found small inverse BC effects that are irreversible, whereas for the C-T phase transition at Curie temperature $T_C \sim 400$ K, we found larger inverse BC effects that are reversible. Our observation of reversible BC effects near the Curie temperature of BTO should inspire studies of BC effects in a wide range of ferroelectric materials. This should expand the range of BC materials beyond ammonium sulphate and a small number of magnetic materials allowing caloric properties to be exploited in cooling devices without the electrical breakdown that limits EC effects.

See supplementary material for Figures S1, S2, and S3. All relevant data are presented via this publication and supplementary material.

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