The Impact of Hysteresis on the Electrocaloric Effect at First-Order Phase Transitions

Madhura Marathe, Claude Ederer, and Anna Grünebohm

We show that this irreversibility can be overcome by using larger fields.

1. Introduction

The electrocaloric (EC) effect results in an adiabatic temperature change (or an isothermal entropy change) with variation of an external electric field.\cite{1,2} Along with the magnetocaloric and elastocaloric effects, the EC effect has the potential to lead to energy-efficient and environmentally friendly solid-state cooling devices.\cite{3,4} Typically, the largest caloric response is observed near ferroelectric phase transitions.\cite{5} In particular, giant temperature changes have been found at first-order (FO) phase transitions with coupled ferroic and structural degrees of freedom.\cite{6,7} However, close to FO transitions, a coexistence region exists, which leads to thermal hysteresis, i.e., within a certain temperature range, the system can exist in different (meta-) stable states depending on the history of the sample. Thus, at the same temperature and applied field strength, the state of the system can differ in field cooled (FC), field heated (FH), zero-field cooled (ZFC), or zero-field heated (ZFH) samples.

The impact of thermal hysteresis on the reversibility of the caloric response has been studied extensively for the case of magnetic materials close to magneto-structural phase transitions.\cite{4–7} It has been shown that for systems with broad hysteresis, a giant caloric response can typically only be found for the first field pulse. However, for cooling applications, a device needs to be operated over a large number of field cycles. Therefore, the search for hysteresis-free materials, ways to bypass the thermal hysteresis, or the use of smaller reversible responses within the coexistence region is a very active area in the field of magnetic materials.\cite{15–17} In contrast, there are only a few such studies for the EC effect. Thus, a better understanding of the impact of thermal hysteresis is needed for future applications of EC materials.

The EC effect has been extensively studied in BaTiO₃ (BTO), see, e.g., Refs. \cite{8–20}. BTO exhibits a paraelectric (PE) cubic (C) phase at high temperatures and, on cooling, undergoes three transitions to ferroelectric (FE) tetragonal (T), orthorhombic (O), and rhombohedral (R) phases. In absence of an external field, each FE transition in BTO is a FO transition.\cite{21} For small fields, this results in thermal hysteresis and coexistence regions, in which the state of the system depends on the preceding heat treatment. Previous studies have shown that under increasing strength of an applied field, the transition temperatures are shifted, the thermal hysteresis is reduced, and for sufficiently large fields the nature of the transition can change.\cite{19,22,23} For the PE–FE transition, there is no well-defined phase transition any more above a critical field strength $E_c$.\cite{21}

Some experimental measurements performed at small applied fields have indeed reported irreversibility in the EC response of BTO. For example, Moya et al.\cite{9} have found an irreversible EC response at the PE–FE transition. Furthermore, around the FE–FE (T–O) transition, Bai et al.\cite{10} measured a large EC response only during the first application of an electric field, which was then reduced to a rather small response on further cycling, analogous to the irreversibility found at magneto-structural phase transitions.\cite{6,7}

Most theoretical studies so far have focused on the EC effect close to the PE–FE transition under large fields. Since at large fields ($E > E_c$) there is no FO phase transition,\cite{11,19} irreversible effects are not expected in this case. On the other hand, an irreversible EC effect has been predicted even for large fields,
when different metastable states occur in defect-doped BTO.\[17]\nUnder small fields, thermal hysteresis exists at all transitions, and thus an irreversible EC effect is expected, which depends strongly on the thermal history of the sample.

In this paper, we study the EC response of BTO at applied fields that are smaller than the critical fields. In particular, we examine how the EC effect depends on the thermal history of the sample, and whether periodic cycling of the field near the coexistence region results in irreversibilities. To this end, we perform molecular dynamics (MD) simulations for an effective Hamiltonian derived from first principles (see, e.g., Ref. \[18\]). We focus on the EC response around the C-T and T-O transitions. We first show that, within the coexistence region, the EC temperature change indeed depends on the initial phase of the system. Then, we study the EC response for different applied field strengths around the critical field while switching the field on and off. Further, we apply a field for up to two cycles at a few selected temperatures to examine the reversibility of the response. We observe that the effect is irreversible for small fields, with a large response in the first cycle, which then reduces by an order of magnitude in the following cycle. Finally, we briefly compare the observed behavior to the well-known hysteretic effects in materials showing a FO magneto-structural phase transition.

### 2. Computational Details

To construct the effective Hamiltonian used in our work, the atomic degrees of freedom in each unit cell \( i \) are mapped on a ferroelectric soft mode vector \( \mathbf{u}_i \) and a local strain \( \mathbf{w}_i \), see Figure 1(a).\[24,25\] The total energy of the system is then expressed as a low order polynomial in terms of these variables. All parameters of this effective Hamiltonian have been calculated using ab initio density functional theory.\[26\] This method reproduces the correct sequence and order of all three FE phase transitions of BTO as well as the field and temperature dependence of many physical properties without any empirical input, see, e.g., Refs. \([20,19,24–26]\). However, the transition temperatures of BTO are underestimated, as discussed in detail in Ref. \([27]\).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{(a) Illustration of the construction of the effective Hamiltonian: the local atomic arrangement is mapped on the local soft mode vectors \( \mathbf{u}_i \) and the local strains \( \mathbf{w}_i \) in each unit cell. (b)–(c) Illustration of the direct simulation of the EC temperature change: the system is equilibrated in an external field \( \mathbf{E}_i \) at the start temperature \( T_i \), the field is ramped up or down to the final field \( \mathbf{E}_f \) and after equilibrium is reached, the final temperature \( T_f \) is recorded. \( \Delta T \) indicates the adiabatic temperature change on varying the field. For normal EC response, \( \Delta T \) is negative when the field is ramped down (b) and positive when the field is ramped up (c).}
\end{figure}

Nevertheless, the method provides a powerful tool to analyze physical mechanisms and has been successfully used to obtain qualitative trends as well as orders of magnitude of EC response, see, e.g., Refs. \([14–20,28]\). We use the open-source feram code (http://loto.sourceforge.net/feram/\[29\]) which allows to perform MD simulations for the effective Hamiltonian at finite temperatures and fields. We use a \( 96 \times 96 \times 96 \) supercell to simulate bulk BTO within periodic boundary conditions. For computational efficiency, we treat only the soft mode variables as dynamical variables whereas the local and global strains are optimized in each MD step according to the current soft mode configuration.

We calculate the response in bulk BTO using the direct method. First, we allow the system to equilibrate at a given initial temperature \( T_i \) and initial field \( \mathbf{E}_i \) using sufficiently long thermalization times in the MD simulations. Then, the applied electric field is either switched off (ramp down) or on (ramp up), as illustrated in Figure 1(b) and (c), respectively. In this study, we always apply the field along the pseudo-cubic [001] direction. During and after the field-ramping, we allow the system to evolve and then equilibrate again within the constant energy (microcanonical) ensemble before averaging the physical quantities of interest. The corresponding EC temperature change \( \Delta T \) is obtained as difference between the initial and final temperatures. Note that the effective Hamiltonian results in a reduction of degrees of freedom from 15 in the real system to 3 in the model system. Therefore, the change in temperature is rescaled by a factor of 1/5. More details of our calculations are described in Refs. \([18,19]\).

To study the impact of thermal hysteresis, i.e., the thermal history of the sample, we prepare the system by either heating or cooling simulations under a constant external field. At each temperature \( T \), local dipole configurations are obtained after thermalization and then used as initial configuration to calculate the EC temperature change. In addition, we have also performed simulations where the starting configuration was obtained by simply randomly initializing the local dipoles and subsequent thermalization at a given temperature and field, ensuring that the system is in a well-defined initial state, before ramping the field either up or down from a given initial temperature and monitoring the asymmetry of the obtained EC temperature change.

### 3. Results and Discussion

First, we investigate the influence of the thermal history on the EC effect of BTO. We calculate the EC response for ramping down a field of \( \mathbf{E}_i = 20 \text{ kV cm}^{-1} \) applied along [001] near the C-T and T-O transitions. This field strength is below the critical field strength found for our model and thus there is thermal hysteresis at both transitions (even though at the C-T transition it is rather narrow).\[19\] To determine the influence of the thermal history, we perform two simulations for each \( T_i \), using the two starting configurations obtained from FH and FC simulations.\[1\]

The calculated \( \Delta T \) as function of initial temperature is plotted in Figure 2(a) and (c). We observe a clear difference between the EC response calculated for the FH and FC starting

\[1\] Note that we model an ideal system without defects, inhomogeneities, or electrodes, which may promote the nucleation of the first order phase transition, and we thus obtain more pronounced hysteretic effect compared to what is typically observed in real samples.\[19\]
leads to a reduction or vanishing of (induced) polarization, but the are the same in both cases, for \( T < 304 \text{ K} \). At the T–O transition, we obtain a sharp peak at 135 K for the FC case with \( \Delta T \approx 1.3 \text{ K} \). The response is inverse, i.e., positive \( \Delta T \) under field removal, as expected for this transition and field along [001], see Ref. [19]. For the FH case, we observe only a small feature around 170 K with a magnitude of \( \approx 0.12 \text{ K} \) and a broad decrease toward the low-T side.

To better understand these differences between the FC and FH response, Figure 2(b) and (d) shows the components of the electric polarization along the applied field direction as function of initial temperature for the initial and final states, respectively, i.e., with and without applied field. One recognizes that the difference in the FC and FH EC response is related to differences in the initial and/or final states of the system. At the PE–FE (C–T) transition, the FH initial configurations are in the FE-T phase up to \( T_1 = 306 \text{ K} \), whereas in the FC case, the system is initially in the FE-T phase only for \( T_1 \leq 304 \text{ K} \), indicating the (narrow) thermal hysteresis for this field strength. Consequently, the corresponding EC response differs for 304 K < \( T_1 \leq 306 \text{ K} \). The final states after field removal are the same in both cases, for \( T_1 < 304 \text{ K} \) the system ends up in the FE phase, whereas for \( T_1 \geq 304 \text{ K} \) it ends up in the PE phase with zero polarization. Thus, one also recognizes that the large EC response with \( \Delta T > 2 \text{ K} \) occurs only in those cases where the system undergoes a transition from the FE to the PE phase under field removal. In all other cases the removal of the electric field only leads to a reduction or vanishing of (induced) polarization, but the system does not undergo a phase transition. In these cases the EC response is much smaller (\( \Delta T \leq 1 \text{ K} \)).

Conceptually, the EC response can therefore be divided into two different contributions — i) a continuous part, resulting from changes of polarization and entropy induced by the applied field without triggering a phase transition, and ii) a discontinuous transitional part related to the jump of entropy related to the field-induced FO phase transition. The analysis of Figure 2(a) and (b) shows that for fields of the order of 20 kV cm\(^{-1}\) the large EC response of BTO can mainly be attributed to the transitional part (ii), whereas the continuous part (i) is very small.

The same holds true at the T–O transition. For the FC simulations, the large peak in \( \Delta T \) occurs at \( T_1 = 135 \text{ K} \), i.e., on the low temperature side of the coexistence region, when the system can undergo a phase transition from T to O under field removal. This can be seen from the polarization components in the initial and final states shown in Figure 2(d). At all other temperatures, no phase transition occurs, and the EC response is negligibly small. For the FH starting configurations, the system is initially in the O phase up to the (field-dependent) high-T side of the coexistence region. As an applied field of 20 kV cm\(^{-1}\) is not sufficient to shift this phase boundary below the ZFC transition temperature, the system remains in the O phase under field removal. Thus, no phase transition occurs and the EC response remains small over the whole temperature region around the T–O transition. The small feature in \( \Delta T \) below 170 K, i.e., just below the FH T–O transition, is due to an enhanced polarization induced by the applied field. We note that the field-dependent phase transition lines are rather steep (see Ref. [19]) and thus the temperature ranges where a field-induced transition can occur under small fields are extremely narrow. Thus, whether we obtain one or more data points with a phase transition strongly depends on the T-sampling.

Up to now, we have examined how the thermal hysteresis affects the EC response at both C–T and T–O transitions only under field removal. Next, we compare the EC effect under field application and removal, respectively, thereby focusing on the PE–FE (C–T) transition and also considering the impact of the strength of the applied field. In this case, we do not explicitly distinguish FC, FH, ZFC, and ZFH cases. Instead, we simply use starting configurations which have been obtained after random initialization of the local dipoles and subsequent thermalization at the initial temperature \( T_i \), either with or without applied field. Figure 3 shows the resulting EC temperature change as function of \( T_i \) for several applied field strengths. The data-sets with positive \( \Delta T \) correspond to application of the field (“on”), whereas the data sets with negative \( \Delta T \) correspond to removal of the field (“off”). Two main features can be recognized: i) for small fields (\( E_{app} < 50 \text{ kV cm}^{-1} \)) the magnitude and shape of the peaks in the EC effect differ significantly between the “on” and “off” cases, and ii) for larger fields (\( E_{app} = 50 \text{ kV cm}^{-1} \)) the \( \Delta T \) curves look similar for the “on/off” cases but are shifted against each other on the temperature axis. This latter effect can easily be understood from the condition for a completely reversible EC cycle (see Ref. [18]):

\[
\Delta T_{off}(T_i + \Delta T_{on}(T_i)) = -\Delta T_{on}(T_i),
\]
and thus has nothing to do with hysteretic effects. Here, \( \Delta T_{\text{off}} \) and \( \Delta T_{\text{on}} \) correspond to the EC temperature changes under field removal and application, respectively. Note, however, that Eq. (1) is not directly applicable to the data shown in Figure 3, since \( \Delta T \) has been corrected according to the reduced number of degrees of freedom within the effective Hamiltonian (see Section 2). Therefore, the shift in the peak positions in Figure 3 appears to be much larger than the magnitude of \( \Delta T \).

To better understand the difference between the “on” and “off” cases for small applied fields, we also analyze the field-induced change in polarization, \( \Delta P \):

\[
\Delta P = P_i(T_f, E_f) - P_i(T_i, E_i).
\]

Here, \( P_i \) and \( P_f \) denote the polarization in the initial and final states, i.e., before and after the field ramping. Figure 4(a) and (b) depict \( \Delta P \) as function of applied field for a few selected temperatures around the peak in \( \Delta T \) for the “on” and “off” cases, respectively.

We first notice that for the “on” case (i.e., with \( E_i = 0 \)) our random initialization procedure has put the system in the FE phase for all temperatures below \( T_i = 284 \) K and in the PE state for all temperatures above that. Therefore, below 284 K, application of an electric field leads only to minute changes in polarization, since the system is already initially in the FE state (see, e.g., data for \( T = 280 \) K in Fig. 4(a)). Consequently, the EC effect is very small at this temperature. At temperatures slightly higher than 284 K, e.g., at \( T = 288 \) K, the system is initially in the PE state, but even a small field of 12 kV cm\(^{-1}\) can trigger the FO phase transition to the FE state, leading to a steep rise in \( \Delta T \) due to the large transitional contribution to the EC effect. Further increasing the field strength at this temperature results only in a small further increase of \( \Delta T \), due to an increased continuous contribution. At even higher temperatures, closer to the ZFH transition temperature, e.g., at \( T = 296 \) K, a small field of 12 kV cm\(^{-1}\) is not sufficient any more to trigger the transition from the initial PE state into the FE phase. Note that while the system is still in the coexistence region, here, the free energy of the PE state is already significantly lower than that of the FE state. Thus, the EC peak for small applied fields is cut off on the high-T side. Finally, for temperatures above the coexistence region, the EC effect increases monotonously with the applied field strength. This is due to the high polarizability of the PE phase in this temperature and field region close to the phase transition, which leads to an increasingly large contribution from the continuous part and a broadening of the EC response toward higher temperatures. The resulting characteristic peak shape with a sharp drop toward the low-T side and a field-dependent broad shoulder toward higher temperatures has also been observed experimentally in Ref. [13].

The “off” case is rather different from the “on” case, in particular for small fields. For the smallest applied field of 12 kV cm\(^{-1}\), the EC response is essentially negligible at all temperatures. In this case, the random initialization with subsequent thermalization in the applied field has created a FE state for all temperatures below the ZFH transition temperature and a PE state above that. Thus, under field removal the system

\[^2\]We note that for a ZFC starting configuration, the steep rise on the low-T side of the EC peak occurs exactly at the ZFC transition temperature, while in the present case with random initialization it occurs somewhere within the zero field coexistence region.
stays in its initial state (either FE or PE) and no phase transition occurs (at least) for the T-sampling used in our calculations. For the next highest field of 20 kV cm\(^{-1}\) there is a sharp peak with \(|\Delta T| \approx 2.6 \text{ K}\) at \(T_1 = 304 \text{ K}\), which is the only temperature for which a transition from the FE to the PE phase occurs under field removal for this initial field strength (cf. Figure 4). This case is essentially identical to the case shown in Figure 2(a) and already discussed above (note that for 20 kV cm\(^{-1}\) the width of the coexistence region at the C-T transition is only about 2 K and thus the difference between FC, FH, and random initialization is not very crucial). For fields larger than 20 kV cm\(^{-1}\), the field strength approaches the critical field, above which there is no clear difference between FE and PE states. Instead, the system is highly polarizable and the EC peak broadens toward the higher temperature side for increasing field strength, similar to that can be observed for the “on” case. Thus, for fields above \(E_1\) the EC response becomes fully reversible, in the sense of Eq. (1), and the continuous part of the EC effect becomes dominant over the part related to the FO transition entropy.

Toward the low-T side the EC peak exhibits a sharp drop, which is related to the stabilization of the FE phase for zero field. In the “off” case, this occurs when the system cools down during field removal and enters the coexistence region without undergoing a phase transition to the PE state. As the continuous contribution to \(\Delta T\) increases with increasing field strength, this low-T side of the EC peak is shifted toward higher temperatures with increasing field. Note that this shift is overestimated in our simulations due to the overestimation of the unscaled \(\Delta T\), as already discussed in Section 2. This effect also leads to the non-monotonous behavior of \(\Delta P\) at \(T = 304 \text{ K}\) seen in Figure 4(b), where for fields above 25 kV cm\(^{-1}\) the system remains in the FE state under field removal.

Summarizing the discussion related to Figure 3, we find a reversible EC response for fields above the critical field strength for the FO PE-FE phase transition, whereas a strong difference (both in peak height and width) is observed between the “on” and “off” cases for small fields. This is in good agreement with experimental observations for BTO single crystals presented in Ref. [9].

Finally, we examine the (ir-)reversibility of the EC response under field cycling near the maximum EC response close to the PE-FE (C-T) transition. Figure 5 shows the time evolution of the system temperature and polarization as an external field of \(E_{app} = 12 \text{ kV cm}^{-1}\) is applied and removed periodically during the course of the MD simulation starting from an initial temperature of \(T_1 = 304 \text{ K}\). Here, the system is initially in the PE-C phase, which transforms to the FE-T phase during the first application (ramp on) of the field. This results in a large EC temperature change, originating from the transitional contribution due to the FO phase transition (plus a small continuous part).\(^3\) However, on further field cycling the system always stays within the coexistence region, both with and without applied field, and thus it remains in the FE phase. Consequently, one observes only a much smaller EC response related to the continuous contribution. Thus, an irreversible heating of the system occurs during the first field field pulse, whereas a reversible but much smaller response appears during subsequent cycles. This is analogous to the magnetocaloric response observed at FO magneto-structural transitions, e.g., in Heusler alloys.\(^[6]\) There, a large response is found only during the first field pulse, followed by a small but reversible response in subsequent cycles.

4. Conclusions and Outlook

We have used ab initio-based MD simulations for the prototypical ferroelectric material BTO to demonstrate several examples of irreversibility and the impact of thermal hysteresis on the EC response close to FO phase transitions. We found a large EC response, even for small applied electric fields, for cases where the system undergoes a FO phase transition. However, this can depend strongly on the thermal history of the sample and whether the EC effect is measured under field application or removal.

Although at the C-T transition the coexistence region is narrow, a large difference between the EC responses observed under field application and removal, respectively, can occur at small fields. In particular, a large irreversible heating can arise during the first field application. This shows that one should compare the EC response only for well defined initial states (FC, FH, ZFC, or ZFH). Strictly speaking, one should measure the response for several field cycles in order to ascertain the reversible response. However, the response measured on field removal from initially prepared FC and FH states for conventional and inverse response, respectively, can already

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\(^3\) Note that the temperature differences obtained from the system temperature shown in Figure 5 need to be rescaled to obtain the correct \(\Delta T\), as described in Section 2.
give good estimates. In these cases an irreversible transition from a metastable initial state within the coexistence region is avoided in the measurement.

At the T–O transition, the coexistence region is much broader, resulting in a nearly vanishing response in the FH case, since a small field is not sufficient to trigger the FO phase transition from the O to the T phase. Thus, a reversible cycling across the T–O transition requires significantly larger field strengths.

Generally, for small fields the main contributions to the EC response results from the discontinuous transition entropy when crossing the FO phase transition, whereas the continuous part is small but increases with increasing field strength. For the PE–FE (C–T) transition, the continuous part becomes dominant above the critical field strength \(E_c\), and at temperatures above the ZFH transition temperature. Therefore, hysteretic effects can be avoided by using sufficiently large applied fields, or by cycling the system above the ZFH transition temperature. In contrast, the continuous contribution to the EC effect is small within the PE phases near the T–O transition. We also note that, while a reversible cycling across the T–O transition is in principle possible for very large fields, a partial cancelation between transitional and continuous parts can occur, since these two contributions can have opposite signs.[19]

We note that the EC effect at the T–O transition shows several analogies to the well known giant magnetocaloric effect found at magneto-structural phase transitions, e.g., in Heusler alloys.[7] There, a giant response is typically found for the first field pulse only, and the system stays within the coexistence range and shows a much smaller but reversible response under further field cycling. Furthermore, the structural (transitional) and magnetic contributions to the magnetocaloric effect are opposite in sign,[19] similar to what can also occur a T–O transition in BTO, as stated above. For the case of the magnetic materials, it has been shown that it is possible to bypass the hysteresis through an additional stimulus, such as, e.g., hydrostatic pressure.[5] The same is also possible for EC materials exhibiting strong hysteretic effects as reported by Stern-Taulats et al. for BTO.[31]

As our model is based on a defect-free homogeneous system, it allows to clearly isolate intrinsic and different extrinsic factors (such as, e.g., domains, defects, inhomogeneities, ...) determining hysteretic effects. In the present work, we have focused on intrinsic properties, while the influence of domains, defects, and inhomogeneities can be incorporated in future studies. Our simulations therefore provide a good reference for comparison and analysis of future experimental investigations of hysteretic effect in EC materials.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

BaTiO\(_3\), electrocaloric effect, first-order phase transitions, hysteresis, molecular dynamics simulations

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