Influence of defects on ferroelectric and electrocaloric properties of BaTiO₃

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We report modifications of the ferroelectric and electrocaloric properties of BaTiO₃ by defects. For this purpose, we have combined ab initio-based molecular dynamics simulations with a simple model for defects. We find that different kinds of defects are no obstacle for a large caloric response and reduce the thermal hysteresis of the ferroelectric transition. For a locally reduced polarization the ferroelectric transition temperature and the adiabatic response are slightly reduced. For polar defects an intriguing picture emerges. The transition temperature is increased by polar defects and the temperature range of the large caloric response is broadened. Even more remarkable, a giant inverse caloric effect has been observed for the first time.

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1. INTRODUCTION

As conventional cooling is presently one of the main carbon dioxide sources, more advanced technologies are urgently needed. In the last years the electrocaloric effect (ECE) has come into focus as a promising new cooling mechanism.¹⁻¹²

Although the change of temperature in a ferroelectric material due to a varying electrical field is known for decades, giant caloric responses up to 12 K have been obtained only recently.¹¹ The understanding of the ECE is still quite unsatisfactory. Materials with a large and reversible adiabatic response in a proper temperature range, and which are ecologically save and economically viable, have to be found.

Also, so far little is known about possible limitations of the ECE due to defects. However, defects such as missing oxygen atoms or impurities and dopants are common in ferroelectric materials. They influence remanent polarization and polarization switching, which are important for the caloric response. In addition defects may induce fatigue effects. Different experimental and theoretical studies deal with the modification of ferroelectrics by doping.⁶⁻¹¹ Evidently, even the modification of the ferroelectric phase diagram under such doping is still unclear. For example, reduction, insensitivity, and increase of the ferroelectric transition temperature in BaTiO₃ (BTO) due to doping have been found.⁵¹¹

In particular, experimental and theoretical investigations reveal the important role of transition metal doping on fatigue behavior in ferroelectric perovskites.¹²⁻¹⁷ It has been found that an internal bias field builds up in field polarized (poled) Cr doped BTO, which could be related to the alignment of defect dipoles with the overall polarization.¹² In this context Erhart and co-workers performed detailed ab initio based transition state theory simulations on transition metal doped perovskites.¹²⁻¹⁷

They found that polar O-vacancy dopant complexes, which induce local dipoles, form immediately. It is most favorable if these dipoles align parallel to the overall polarization. However, their relaxation is rather slow and the defect dipoles thus give rise to aging and fatigue, i.e. broadening and shift of the field hysteresis. These changes may largely modify the caloric response and its reversibility. Even though the reduction of the ECE in BTO by micro-cracks has been discussed in Ref. ¹⁸, we are not aware of any systematic investigation on the influence of doping and defects on the ECE. A large ECE of 0.5 K/300 kV/cm has been found for doped BTO in an industrially manufactured multilayer capacitor.¹⁰

The present paper aims to fill the gap in the understanding and optimization of the ECE. We investigate the effect of local defect dipoles on the phase diagram and the ECE in BTO by means of molecular dynamics simulations employing an effective Hamiltonian based on ab initio parametrization. For the first time, the change of operation range and magnitude of the ECE with different kinds of defects is investigated. Also the influence of different measuring protocols is revealed. With measuring protocol we mean the influence of the sample history, i.e. poled or as-prepared samples, cooling-down or heating-up simulations and the use of unipolar and bipolar electrical fields.

We show that a reduced local polarization reduces \( T_C \), polarization, and the ECE, while local defect dipoles with slow relaxation dynamics and large dipole moment increase \( T_C \) and may even induce large inverse caloric response.

The paper is organized as follows. First, the computational methods and the model for defects are discussed in Sec. 2. In Section 3 the general features of the phase diagram of BTO, the ECE of the ideal material, and the effect of non-polar defects are discussed. Section 4 deals with the influence of polar complex dipoles on the phase diagram of BTO and the ECE for different defects and measuring protocols. Results for the case of disordered dipoles can be found in Sec. 4.4. Finally, conclusions and outlook are given in Sec. 5.
2. COMPUTATIONAL MODEL

Molecular dynamics (MD) simulations have been performed employing the feram code [http://loto.sourceforge.net/feram/](http://loto.sourceforge.net/feram/) developed by Nishimatsu *et al.* [20] based on an effective Hamiltonian

\[
H^{\text{eff}} = \frac{M^*_{\text{dipole}}}{2} \sum_{R,\alpha} \dot{u}_\alpha^2(R) + \frac{M^*_{\text{acoustic}}}{2} \sum_{R,\alpha} \dot{u}_\alpha^2(R) \\
+ V^{\text{self}}(\{u\}) + V^{\text{dip}}(\{u\}) + V^{\text{short}}(\{u\}) \\
+ V^{\text{elas}, \text{ homo}}(\eta_1, \ldots, \eta_6) + V^{\text{elas}, \text{ inho}}(\{w\}) \\
+ V^{\text{coup}, \text{ homo}}(\{u\}, \eta_1, \ldots, \eta_6) + V^{\text{coup}, \text{ inho}}(\{u\}, \{w\}),
\]

(1)

with \(\eta_1, \ldots, \eta_6\) the six components of homogeneous strain in Voigt notation. \(V^{\text{self}}(\{u\})\) is the self energy of the local mode, \(V^{\text{dip}}(\{u\})\) is the long-ranged dipole-dipole interaction, \(V^{\text{short}}(\{u\})\) is the short-ranged interaction between local soft modes, \(V^{\text{elas}, \text{ homo}}(\eta_1, \ldots, \eta_6)\) is the elastic energy from homogeneous strains, \(V^{\text{elas}, \text{ inho}}(\{w\})\) is the elastic energy from inhomogeneous strains, \(V^{\text{coup}, \text{ homo}}(\{u\}, \eta_1, \ldots, \eta_6)\) is the coupling between the local soft modes and the homogeneous strain, and \(V^{\text{coup}, \text{ inho}}(\{u\}, \{w\})\) is the coupling between the soft modes and the inhomogeneous strain.

Instead of treating all atomic positions as degrees of freedom, the collective atomic displacements are coarse-grained by local soft mode vectors \(u(R)\) and local acoustic displacement vectors \(w(R)\) of each unit cell at \(R\) in a simulation supercell. Therefore, the number of degrees of freedom per unit cell is reduced in a first step from 5 atoms times the three cartesian directions (= 15) to 2 three dimensional vectors. \(M^*_{\text{dipole}}/2 \sum_{R,\alpha} \dot{u}_\alpha^2(R)\) and \(M^*_{\text{acoustic}}/2 \sum_{R,\alpha} \dot{w}_\alpha^2(R)\) are the kinetic energies possessed by the local soft modes and the local acoustic displacement vectors along with their effective masses of \(M^*_{\text{dipole}}\) and \(M^*_{\text{acoustic}}\). In a second coarse graining step an internal optimization of \(E(w(R))\) is used reducing the degree of freedom to the three components of the soft mode \(u(R)\). Details of this Hamiltonian are explained in Refs. [19][21].

The set of parameters for the effective Hamiltonian for BaTiO\textsubscript{3} have been obtained by density functional theory simulation at \(T = 0\) K and are listed in Ref. [22].

Within the molecular dynamics (MD) simulations, periodic boundary conditions and a cell size of 96 × 96 × 96 are used unlike otherwise stated. For simulations in the canonical ensemble (NPT), the Nosé-Poincaré thermostat is applied [23] For cooling-down and heating-up simulations on a dense temperature grid of at most 5 K steps, the pre-converged configuration of previous steps is used as input for each temperature step and thus the equilibration time can be reduced to 40,000 fs.

The procedure of direct simulation of the ECE involves three steps: first, constant-temperature MD is performed for a fixed external electric field, \(E\) along [001]. Next, the field is ramped down with a rate of 0.05 kV/cm/fs and simultaneously we change to constant-energy MD in the micro-canonical ensemble that is allowed to evolve using the leapfrog method. The final state at the end of the constant-temperature MD is used as the initial state for the constant energy MD. As last step we monitor the kinetic energy after 10,000 further equilibration steps. A time step of \(\Delta t = 2\) fs is used in both ensembles.

In the Hamiltonian, only the three components of the soft mode vector are explicitly taken into account. Thus, the number of degrees of freedom is reduced from 15 to 3 which in turn reduces the specific heat. Therefore, the change of the kinetic energy is rescaled by 15/3 in order to obtain the adiabatic temperature change, cf. Ref. [24].

Defects are modeled by freezing the local soft mode on random positions to a certain value. A local reduction of polarization by a defect is modeled for the limiting case of non-polar defects. Therefore, the local soft mode amplitude in some cells is frozen to zero, see Fig. 1(a). Defect dipoles with slow relaxation are modeled by dipoles with fixed amplitude and direction, see Fig. 1(b). Thus, we investigate the influence of the modified dipole-dipole interaction by local changes of the polarization. The used course graining procedure does not allow to model atomic relaxations near the defect. In addition, we neglect the direct coupling of defects to the external electrical field and perturbations of the ferroelectric matrix near the defect, e.g., by a modified volume or modified short range interactions.

3. BaTiO\textsubscript{3} AND NON-POLAR DEFECTS

The simulated polarization as function of temperature of BTO is illustrated in Fig. 2. At high temperatures BTO is in the paraelectric cubic perovskite structure. Under cooling, three coupled structural-ferroelectric phase transitions exist, to the tetragonal, orthorhombic, and rhombohedral phases, with spontaneous polarization along [100], [110], and [111], respectively. We find transition temperatures of 275 K, 150 K, and 70 K for cooling-down simulations in qualitative agreement with the experimentally found phase sequence. In addition, spontaneous polarization and strain of all phases as well as the first order character of all transitions are as in experiment [25]. The polarization jumps by about
FIG. 2: (Color online) Polarization as function of temperature of BaTiO$_3$; Red: heating-up simulation; Blue: cooling-down simulation; Black: the sample has been equilibrated in 100 kV/cm and polarization and temperature have been recorded after field removal (ECE protocol). In all cases the polarization along [100], [010] and [001] is shown.

For the ECE protocol the data without pressure correction (dashed black lines) is opposed to results for an external pressure correction of $p = -0.005 T$, treating the acoustic degrees of freedom explicitly, and shifted by 150 K to lower temperatures (black stars).

30 $\mu$C/cm$^2$ at $T_C$ and a pronounced thermal hysteresis is present between cooling-down and heating-up, see Fig. 2. Experimentally, a thermal hysteresis of about 10 K has been found for BTO ceramics. For the chosen cell size we find the coexistence region for the paraelectric to ferroelectric phase transition because we neglect nucleation sites such as defects, surfaces or grain boundaries.

In addition to cooling-down and heating-up simulations the polarization profile as obtained in the ECE measurement is included in Fig. 2 in black. First, the material has been equilibrated in an external field of 100 kV/cm, and after the field has been removed, polarization and temperature have been sampled. The polarization profile in this case mainly coincides with the heating-up simulations.

Despite this excellent qualitative description of the material, all transition temperatures are underestimated by about 100 K within the model and parametrization used in our study, cf. Refs. 21, 22. This may mostly be attributed to the fact that thermal expansion is strongly underestimated in the model. One can partly compensate for this with a semi-empirical effective negative pressure given by $p = -0.005 T$ GPa. By this approach, $T_C$ of the paraelectric to ferroelectric transition increases to about 411 - 436 K under cooling-down and heating-up simulations, thus slightly overestimating experimental values. Apart from this temperature shift, the obtained phase diagram is hardly modified. Especially, the polarization profile as obtained under the ECE protocol without pressure correction (black dashed line) and the data with pressure correction shifted by 150 K (black stars) show qualitatively the same trend, see Fig. 2.

All results presented in the following have been obtained without the semi-empirical correction unless otherwise stated. However, all results have been cross-checked with the effective pressure correction.

The ECE in BTO can be understood by simple arguments. Dipole ordering and magnitude of the local polar off-centering increase if an electrical field is applied, see Fig. 3. The induced polarization vanishes, after the field is removed, see Fig. 4. This reduction is mainly due to an increase of disorder of the local dipoles, i.e. an increase of entropy under isothermal conditions. Under adiabatic conditions, this change in entropy is balanced by a decrease of temperature, cf. Fig. 5. The change of polarization and the corresponding adiabatic temperature change are connected by Maxwell’s relation

$$\frac{dT}{dE} = -\frac{1}{c_E} \left( \frac{\partial P}{\partial T} \right)_E.$$  

The polarization increases by approximately 25 $\mu$C/cm$^2$ above $T_C$ as the field of 100 kV/cm induces a large change of polarization in this temperature range, see Fig. 4. In contrast, the change of polarization by an electrical field along [001] is one order of magnitude smaller within the ferroelectric phases at lower temperatures. Thus, the ECE due to the field induced ferroelectric transition above $T_C$ of the heating-up simulation is largest and a maximal adiabatic temperature change of approximately 3.7 K is obtained. A change of at least 1 K is found in a temperature range of 290–360 K for the chosen field strength, see Fig. 5. It has to be noted that the maximal...
adibatic temperature change increases to 7 K if pressure corrections are taken into account. As discussed in Ref. 2, the ECE always increases with increasing $T_C$, cf. Eqn. 2, and thus the increase of $T_C$ by about 150 K is the most important source of this modification.

So far, all simulations have assumed an ideal bulk material. Local reduction of polarization will occur because of defects, such as oxygen vacancies, grain boundaries and surfaces. This setup is modeled for the limiting case of fully non-polar defects. These "inactive" dipoles reduce the overall dipole-dipole interaction in the system. Thus, the energy gain for a parallel alignment of all dipoles, i.e., a ferroelectric phase with large spontaneous polarization, is systematically reduced. As the free energy (F)

$$ F(T, E) = F_0(T, E) - TS(T, E) \quad (3) $$

rather than the energy ($F_0$), determines the equilibrium state of the system at finite temperatures, the transition temperature is shifted to lower temperatures, see Figs. 3 and 4, since the paraelectric phase has a larger entropy.

Also, the defects systematically reduce tetragonal strain (cf. Fig. 11), strain-dipole coupling energy, and the overall polarization. As the imposed defects may act as nucleation sites, they systematically reduce the thermal hysteresis, see Fig. 5. The steep change of the polarization at $T_C$ and the first order character of the transition are conserved.

As $T_C$ and $dP/dT_E$ are reduced by the non-polar defects, compare lines with stars and squares in Fig. 4, the overall adiabatic temperature change (see Fig. 5) is systematically reduced with the number of defects, cf. Eqn. 2. For example, for $\Delta E = 100$ kV/cm, 5% non-polar defects reduce the ECE by a factor of two and shift the peak of the caloric response by approximately 100 K to lower temperatures. The shape of the $\Delta T(T)$ peak is not considerably modified by the defects. Since especially no broadening of the curves is visible, also the temperature region with a temperature change of at least 1 K is linearly reduced with the number of defects, from approximately 70 K without defects to approximately 45 K for 5% defects.

In summary, non-polar defects reduce the maximal response of the ECE of BTO. However, even 5% defects do not suppress the caloric response and are thus no obstacle for the use of the material in ECE applications. One has to note, that the present model overestimates the effect of local defects as "real" defects most likely correspond to a local reduction of the polarization rather than a complete freezing and thus a smaller shift and reduction of the adiabatic response. In addition, the operation range and the temperature giving maximal adiabatic response can be lowered by non-polar defects.

4. POLAR COMPLEXES

In the present section we discuss the influence of stable local defect dipoles. For example, this setup corresponds to dopant-oxygen vacancy complexes in transition metal doped perovskites. It has been reported that such complexes form immediately during the synthesis process, that they have much slower relaxation times than the free dipoles related to the ferroelectric soft mode, and that different relative orientations towards the spontaneous polarization of the host ferroelectric material are possible. In the present study, we assume fixed defect dipoles, which is a rather realistic approximation at low and ambient temperatures during the time span of a typical ECE measurement, cf. Ref. 15.

Dipoles with a charging of 2 $|e|$ and distance of 1.91 Å have been found for fully equilibrated O vacancy-Cu complexes in PbTiO$_3$. This would correspond to a local polarization of approximately 106 $\mu$C/cm if one defect dipole per BTO unit volume is assumed. Fixed local soft mode amplitudes up to 0.4 Å are taken into account,
corresponding to a locally enhanced spontaneous polarizations of 100 µC/cm at the maximum.

4.1. Unipolar cycling

For ferroelectric perovskites, it has been shown that it is energetically most favorable if the defect dipoles order with the overall polarization of the ferroelectric phase.\cite{Ref. 15, 16} Equilibration to this ground state (aging) can be achieved, e.g., by cooling in a strong external field. If a unipolar external electrical field is used in the ECE measurement, one may assume fixed defect dipoles parallel to the direction of the field for the whole measuring time (switching on and off the field).

The influence of 1% defect dipoles with strengths corresponding to soft mode amplitudes of 0.2 Å (50µC/cm) and 0.4 Å (100 µC/cm) on the phase diagram without and with a parallel external field of 100 kV/cm are illustrated in Fig. 6. The fixed local defect dipoles create an additional internal electrical field and thus the overall polarization and the transition temperature increase with the strength of the defect dipoles and their density. Similarly, an internal bias field has been found experimentally in aged doped BTO.\cite{Ref. 27} There, the hysteresis is shifted along the field axis and the coercive field increases, if the defect dipoles in a doped sample have fully ordered.

It has to be noted that the shift of the transition temperature by 100 K and the magnitude of the internal dipole field overestimate experimental results, e.g., in Ref. \cite{Ref. 27} On the one hand, the used model for defects neglects relaxation effects and domains. One the other hand, it is not ensured that all dopants form fully relaxed dipole complexes in experiment, which anyway forbids a quantitative comparison of the bias field. In addition, we have assumed a maximal defect dipole amplitude of 0.4 Å corresponding to a rather large local polarization of 100 µC/cm which may exceed the dipole moment of the real doped material. However, the same qualitative trends are found for a soft mode amplitude of 0.1 Å. Here, the shift of \(T_C\) and thus the adiabatic response is only 10 K.

If the external field is removed in our simulations, the overall polarization is reduced as discussed in the previous section. However, compared to the ideal system without defects, the remaining polarization is larger. Already for 1% defects with a soft mode amplitude of 0.1 Å the polarization profile is smooth and the thermal hysteresis is smaller than the accuracy of the simulation. This soft mode amplitude corresponds to a local polarization of 25 µC/cm which is even slightly smaller than the free dipoles of the host material.

For an amplitude of 0.2 Å, we find a rather smooth change of polarization with temperature, a vanishing thermal hysteresis, and a large polarization above the critical temperature of the ideal system. Thus, the system shows the characteristic features of a field induced polarization above the critical field strength rather than the first order transition of the ideal system, see Fig. 6.

Although the system cools down under field removal like the defect free material, the fixed dipoles reduce the caloric response. First of all, the smoothing of the polarization profile reduces \(\Delta T\), cf. Eqn. 2. Second, possible contributions by the latent heat of the first order transition are lost as the system is beyond its critical point. In addition, the number of free dipoles is slightly reduced by the defects.

The reduction of the caloric response for 1% defects with a dipole moment corresponding to soft mode amplitudes between 0.1 and 0.4 Å is a factor of two. However, the reduction is independent on the dipole strength, and it is accompanied by a slight broadening of the \(\Delta T(T)\) curve. An ECE of at least 1 K is obtained in a temperature interval of approximately 90 K, respectively 115 K for soft mode amplitudes of 0.2 and 0.4 Å and thus in an even larger interval than for the pure system.

As the polarization profile is shifted to higher temperatures proportional to the strength of the internal dipole
field, one can additionally adjust the optimal temperature of the caloric response by using proper dopants.

Unfortunately, there is no clear picture on the modification of the transition temperature of BTO by doping in experiment. Either an increase, no modification, or even a decrease of $T_C$ have been discussed. Here, besides the pure bulk effect, the dopants tend to reduce the grain size which in turn reduces the transition temperature.

In the simulations, the maximal adiabatic temperature change and the shape of the $\Delta T(T)$ curve are basically the same for different dipole strengths (0.1-0.4 Å) as soon as the internal field exceeds the critical field strength. Complementary to the dipole strength, the density of defect dipoles modifies the induced internal field. Thus, if the number of defects increases, the peak of the adiabatic response for an external field of 100 kV/cm is further reduced, broadened and shifted to higher temperatures.

In summary, unipolar dipole defects pointing along the direction of the external field are no obstacle for a large ECE. For 1% defects still an ECE of approximately 2 K can be found for an external field of 100 kV/cm. In addition the $\Delta T(T)$ curves and thus the operation range of the ECE broadens, which is beneficial for operation.

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In summary, unipolar dipole defects pointing along the direction of the external field are no obstacle for a large ECE. For 1% defects still an ECE of approximately 2 K can be found for an external field of 100 kV/cm. In addition the $\Delta T(T)$ curves and thus the operation range of the ECE broadens, which is beneficial for operation. Only the narrow peak of approximately 10 K width directly at $T_C$ is reduced as the internal bias field is beyond the critical field. Although the used simple model may quantitatively overestimate the shift of the caloric response with temperature, the use of defect dipoles is clearly no obstacle and may even be used to tune the operation range of a ECE device under unipolar cycling.

Depending on measurement protocol and history of the sample, one can also think of metastable defect dipoles pointing antiparallel to the overall polarization for a certain number of unipolar field cycles. Such a setup has exciting consequences for the phase diagram, see Figs. 7 and 8, and the caloric response of the material, see Fig. 9.

Analogous to the discussion in the last section, the defect dipoles induce an internal electrical field. However, this internal field is not homogeneous and its coupling to the free dipoles shows a different temperature dependency than the coupling to the external field. We find three different states depending on temperature, relative strength of external and internal field strength, and simulation protocol.

State 1 corresponds to a ferroelectric state for which all dipoles are aligned with the external field. In state 2 the free dipoles align with the internal field of the defect dipoles and in state 3 external and internal field mainly cancel each other. It has to be noted that all three phases can be reproduced with different random defect distributions and cell sizes. In addition, the use of an external pressure does not modify the phase diagram despite the increase of transition temperature and polarization which as also been discussed for ideal BTO, cf. Figs. 7 and 8.

If the external field clearly exceeds the internal one, the phase diagram shows only a field induced transition from the paraelectric high temperature phase to the ferroelectric state 1. For instance, for 1% defects corresponding to a soft mode amplitude of 0.4 Å within an external field of 500 kV/cm, or for a soft mode amplitude of 0.2 Å in an external field of 100 kV/cm, only the paraelectric state and the ferroelectric state polarized along the field direc-
As this field strength is beyond the critical field no thermal hysteresis is present. The local polarization along small chains of several lattice constants below and above the defect dipoles is coupled to the internal field resulting in a slight reduction of $P$ and the tetragonal strain compared to the parallel alignment of defect and external field. At the same time the field induced transition temperature is reduced by the internal field, see Fig. 8.

If the internal field exceeds the external one, there is a transition from a state with low polarization to the ferroelectric state 2. For instance, for 50 kV/cm applied to 1% defects with 0.4 Å amplitude, the clamping of polarization to the direction of the defect dipoles is found above 220 K for the ECE protocol. Similarly, only weak polarization to the direction of the defect dipoles is found to 1% defects with 0.4 Å amplitude, the clamping of polar electric state 2. For instance, for 50 kV/cm applied transition from a state with low polarization to the ferroelectric state 2, with a low field coupling, the change of entropy and thus the adiabatic temperature change is reduced albeit a finite caloric response also appears in this temperature region.

In summary, the stability region of three phases with pronounced differences of polarization, can be adjusted by the relative strength of the external field and the internal field given by density and magnitude of the defect densities.

If the external field is removed, it is energetically most favorable for the free dipoles to align with the defects, i.e. if the state discussed in the last section for parallel dipoles is reached. However, with decreasing temperature the relaxation slows down and thus the system with polarization along the field direction, may be stuck in this metastable state for typical simulation times. For example, after 500 ps the system relaxes to the energetic ground state at 210 K for defects with 0.4 Å amplitude after the external field of 100 kV/cm has been removed.

For the fully relaxed system, field removal changes the entropy of the dipole system considerably. Especially, for phase 1 and 3, a large change of $P$ under field removal induces a large temperature change, see Fig. 9. For state 2, with a low field coupling, the change of entropy and thus the adiabatic temperature change is reduced albeit a finite caloric response also appears in this temperature region.

In contrast to the defect configurations discussed in Secs. 3 and 4.1 the dipole entropy is smaller without field. Thus, an inverse ECE is found as the system heats up under field removal. The effect is rather large and adiabatic temperature changes up to 4 K are found for state 3 for 1% defects of 0.4 Å amplitude and an external field of 100 kV/cm, see Fig. 9.

If the internal field is smaller, e.g., if dipoles of 0.2 Å amplitude are assumed, the coupling to the external field is rather strong, see Fig. 4. In this case, the system relaxes from state 1 to a fully polarized state along the direction of the internal field. As the polarization in state 1
is reduced due to the antiparallel internal field, this corresponds to a considerable increase of the dipole ordering. As a consequence an adiabatic temperature change of approximately 3 K is found in a broad temperature range below 350 K, see Fig. 9.

Note, that for a dipole strength of 0.4 Å the relaxation from the metastable state 1 also results in an inverse ECE of about 4 K below 300 K, if an external field of 100 kV/cm is removed. Similar ∆T values can even be found below 250 K for extended relaxation time (not shown in Fig. 9). However, for this combination of internal and external field, the metastable state 1 only appears for field-heated or un-poled samples and thus the ECE is not reversible. After the system has reached the stable state 2 with polarization parallel to the defect dipoles in one of the first field cycles the caloric response is reduced below 1 K in the following ones, see blue stars in Fig. 9.

In summary, a large inverse ECE has to be expected in doped BTO over a broad temperature span if the external field and the antiparallel internal field given by dipole strength and density have a similar magnitude. Here, the relative strength between external field and internal field can be used in order to stabilize one or the other phase within the external field thus adjusting the magnitude and even the sign of the ECE.

### 4.3. Bipolar cycling

Most device concepts so far are based on the bipolar cycling of an electrical field. For such a setup “de-aging” of the sample is present i.e. the internal bias field discussed for fully polarized samples with defects, vanishes with time. It has been discussed in literature that the slow defect dipoles cannot follow the electrical field and are thus exposed to a surrounding polarization pointing half times up and down. As consequence, also half the defect dipoles point in either field direction.

In the following, we assume fixed defect dipoles pointing randomly either parallel or antiparallel to the external field with a 50:50 distribution. For 1% defects corresponding to a local soft mode of 0.4 Å the transition temperature under cooling-down increases by approximately 30 K compared to the ideal system, see Fig. 10.

Furthermore, the local defects act as kind of precursor and thus the thermal hysteresis between cooling-down and heating-up simulations is reduced to at most 5 K. It has to be noted that the overall polarization is reduced under cooling for the configuration shown in Fig. 10 as 180° domains with up and downwards polarization are formed. However, the local soft mode, as well as the tetragonal ratio is very similar between cooling-down and heating-up, see Fig. 11.

One important mechanism for the shift of $T_C$ can be found in the coupling between local strain and local soft mode. Thus, a tetragonal distortion is induced near the polar defects i.e. the lattice constant along the local dipole direction increases compared to the ideal system for all temperatures, see Fig. 11. This tetragonal distortion stabilizes the ferroelectric phase, the energy barrier for the ferroelectric transition is reduced, and $T_C$ as well as the saturation polarization increase. If the in-plane lattice constants are clamped to their bulk value, the defect induced strain is reduced and also the shift of $T_C$ to higher temperatures does not show up anymore in simulations of the material with frozen defects.
The influence of a unique distribution of 1% dipoles corresponding to a soft mode amplitude of 0.2 Å along all cubic directions is illustrated in Fig. 12. Heating-up and cooling-down simulations including a temperature dependent pressure correction have been performed. The jump of the polarization at $T_C$ is steep and a thermal hysteresis is present, i.e. the first order character of the FEL transition is conserved. Here, only one sixth of the dipoles point parallel or antiparallel to the external field. This results in rather small internal fields along a certain direction. In addition, the dipole fields should in average cancel each other. In contrast to the example of dipoles pointing along and antiparallel to the overall polarization, no direction for the tetragonal strain is favored by the defect dipoles and thus $T_C$ is not shifted to higher temperatures. Instead, the magnitudes of $P(T_C)$ and $T_C$ are reduced by the doping similar to 1% non-polar defects and thus a slightly reduced ECE has to be expected.

In summary, the equal distribution of defect dipoles along all cubic lattice directions in an as-prepared cubic sample may slightly reduce the ECE. However after several ECE cycles, the defect dipoles would most likely equilibrate with the direction of the applied field and the ECE as discussed in Sec. 4 would recover.

One may also think of an equilibrated sample with all defect dipoles pointing perpendicular to the external field at the beginning of an ECE measurements. For 1% defect dipoles of 0.4 Å soft mode amplitude in an perpendicular field of 100 kV/cm, the free dipoles couple to the frozen defects rather than to the external field, cf. Sec. 4.1. We thus find a tiny induced polarization parallel to the external field and only a negligible adiabatic response. In addition, perpendicular defect dipoles couple to the local strain perpendicular to the external field, i.e. the lattice constant parallel to the external field is even reduced compared to the ideal system further destabilizing the ferroelectric order along the direction of the external field.

If the ratio between external field and internal dipole field changes, e.g., by a reduction of the dipole strength, the coupling of the system with the external field increases. For instance, the free dipoles align with an external field of 100 kV/cm in the presence of 1% perpendicular defects with a soft mode amplitude of 0.1 Å. However, even for these weaker dipoles, the polarization aligns with the defect dipoles for low temperatures again (below 280 K). Although the polarization along the field direction changes considerably for 0.1 Å dipoles when the field is removed, this is mainly related to a rotation rather than a change of $|P|$ which determines the adiabatic temperature change in Eqn. 2. Although a peak of the adiabatic temperature change exists at the same temperature as for the ideal system, the peak width is considerably reduced, the maximal response for 100 kV/cm accounts to 0.8 K, only, and the response changes sign at 280 K. In conclusion the appearance of a large number of perpendicular defect dipoles may hamper a large caloric

As no net internal field builds up for the equal distribution of both kind of defects, the polarization shows a steep jump at $T_C$ for heating-up simulations or the ECE protocol. Analog to the ideal system, an external field induces a spontaneous polarization, resulting in large adiabatic temperature change above the transition temperature. However, the dipoles slightly reduce the adiabatic response at its peak maximum. This effect is similar to 1% non-polar dipoles but a slightly broader peak is found and the adiabatic response exceeds 1 K between 270 and 350 K.

In summary, a large adiabatic response can be obtained for all relative orientations between local defects and external field, tested so far. Especially, the dipole distribution under an cycling external field is no obstacle for the ECE. The operation range is even broadened in comparison to the ideal system and it is slightly shifted to higher temperatures. Antiparallel defects have exciting consequences as even the sign of the ECE can be changed and a large adiabatic response can be stabilized over a wide temperature range i.e. at least of 100 K for 0.2 Å i.e. about 50 μC/cm² dipole strength in an external field of 100 kV/cm.

4.4. Disordered dipoles

For the as-prepared cubic sample, the alignment of defect dipoles along all cubic lattice direction has the same energy and probability. In the following we discuss the influence on the phase diagram and the ECE by defect dipoles perpendicular to the applied field.
TABLE I: Summary of the influence of different kind of defects on the phase diagram and caloric response as obtained within our ab initio based molecular dynamics simulations.

| Impurity                                        | $T_C$   | ECE          | thermal hysteresis |
|------------------------------------------------|---------|--------------|--------------------|
| non-polar defect or locally reduced polarization| reduced | reduced      | reduced            |
| polar defects parallel to external field        | increase| broadening of $\Delta T(T)$ | vanishes           |
| 50:50 distribution of parallel and antiparallel defects | increase| inverse broadening of $\Delta T(T)$ | different metastable |
| antiparallel defects in unipolar field          | increase| inverse broad range | states             |
| randomly ordered dipoles                        | reduced | reduced      | reduced            |

response. As a consequence, only fully equilibrated defect rich samples should be taken for ECE measurements and the field direction has to be held constant during cycling in order to achieve a maximum caloric response.

5. CONCLUSIONS AND OUTLOOK

We have discussed the influence of different defects on the ferroelectric and electrocaloric properties of BTO in the framework of ab initio based molecular dynamics simulations. The main influences of different kinds of defects are summarized in Tab. I.

We find that defects with locally reduced polarization tend to reduce $T_C$ and the adiabatic response. The same trend is found for strong defect dipoles with slow relaxation, but without a preferred alignment. However, in both cases the reduction of the ECE is only small for the tested defect concentrations and thus does not contradict a use of BTO in ECE cooling devices.

In addition, we have discussed the possible benefit of dopants for the ECE. For this purpose we have simulated the influence of fixed defect dipoles on the ECE systematically. Dipoles pointing along the tetragonal axis of BTO tend to increase $T_C$ which could partly be related to the strong dipole-strain coupling. If the defect dipoles, or at last half of them, are pointing parallel to the external field, the caloric response is slightly reduced and the $\Delta T$ curve is shifted to higher temperatures and broadens. Such kinds of defect dipoles are beneficial for applications based on ferroelectric materials as they open up a possibility to broaden the operation range.

Excitingly, the doping of BTO samples may even induce a giant inverse ECE under certain measurement protocols. Our investigation have shown that defect dipoles pointing antiparallel to the external field form an internal electrical field which couples to the free dipoles with a different temperature dependency than the external field. The relative strength between internal and external field at a certain temperature can be adjusted, e.g., by the number and strength of the imposed defect dipoles. If the field is removed, the free dipoles align again with the defect dipoles resulting in a reduced entropy and thus a heating of the sample for all these states. Especially, for one high-temperature state which can be found for different combinations of internal and external field, the polarization within the external field is quenched below $T_C$, resulting in a giant inverse caloric response under field removal.

Future work will concentrate on improved modeling of the influence of defects, e.g. by using slowly relaxing but dynamic defect dipoles. In addition, the combination of defects with alloying is promising with respect to adjusting the operation temperature for possible applications.

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1. X. Moya, S. Kar-Narayan, and N. D. Mathur, Nature materials 22, 439 (2014).
2. M. Marathe and C. Ederer, App. Phys. Lett. 104, 212902 (2014).
3. Y. Bai, G.-P. Zheng, K. Ding, L. Qiao, and S.-Q. Shi, J. Appl. Phys. 110, 094103 (2011).
4. S. P. Beckman, L. F. Wan, J. A. Barr, and T. Nishimatsu, Mater. Letters. 89, 254 (2012).
5. M. Ožbolt and A. P. A. Kitanovski and, J. Tušek, Int. J. Refrig. 37, 16 (2014).
6. I. Ponomareva and S. Lisenkov, Phys. Rev. Lett. 108, 167604 (2012).
7. J. F. Scott, Annu. Rev. Mater. Res. 41, 229 (2011).
8. H.-J. Hagemann, J. Phys. C.: Solid State Phys.: 11, 3333 (1978).
9. M. Maglione, R. Böhmer, A. Loidl, and U. T. Höchli, Phys. Rev. B 40, 11441 (1989).
10. S. Kar-Narayan and N. D. Mathur, J. Phys. D: Appl. Phys. 43, 032002 (2010).
11. R. Maier, J. L. Cohn, J. J. Neumeier, and L. A. Bendersky, App. Phys. Lett. 78, 2536 (2001).
12. H. Neumann and G. Arlt, Ferroelectrics 76, 303 (1987).
13. C. H. Park and D. J. Chadi, Phys. Rev. B 57, R13961 (1998).
14. Y.-K. Choi, T. Hoshina, H. Takeda, and T. Tsurumi, Jpn. J. Appl. Phys 50, 031504 (2011).
15. P. Erhart, P. Träskelin, and K. Albe, Phys. Rev. B 88, 024107 (2013).
16. P. Erhart, R.-A. Eichel, P. Träskelin, and K. Albe, Phys. Rev. B 76, 174116 (2007).
17. P. Erhart and K. Albe, Appl. Phys. Lett. 102, 084111 (2007).
18. Y. Bai, X.-C. Zheng, and L. Qiao, Sci. Rep. 3, 2895 (2013).
19. T. Nishimatsu, U. V. Waghmare, Y. Kawazoe, and D. Vanderbilt, Phys. Rev. B 78, 104104 (2008).
20. R. D. King-Smith and D. Vanderbilt, Phys. Rev. B 49, 5828 (1994).
21. W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. B 52, 6301 (1995).
22. T. Nishimatsu, Y. K. M. Iwamoto, and U. V. Waghmare, Phys Rev B 82, 134106 (2010).
23. S. D. Bond, B. J. Leimkuhler, and B. B. Laird, J. Comp. Phys. 151, 114 (1999).
24. T. Nishimatsu, J. A. Barr, and S. P. Beckman, J. Phys. Soc. Jpn. 82, 114605 (2013).
25. A. Kumar and U. V. Waghmare, Phys. Rev. B 82, 054117 (2010).
26. T. Kanata, T. Yoshikawa, and K. Kubota, Solid State Communications. 62, 765 (1987).
27. G. Arlt and H. Neumann, Ferroelectrics 87, 109 (1988).
28. This rather fast variation of the field already results in a convergency of $\Delta T$ better than 0.3 K.
29. It has to be noted that instantaneous field removal and an explicit treatment of the acoustic degrees of freedoms have been used in connection with the pressure correction.