Tuning the caloric response of BaTiO$_3$ by tensile epitaxial strain

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Abstract – We investigate the effect of epitaxial strain on the electrocaloric effect (ECE) in BaTiO$_3$ by means of ab-initio–based molecular-dynamics simulations. We show that tensile strain can be used to optimize the operation range for ferroic cooling. Strain in the range of $\leq 1\%$ can be used to shift the operation temperature by several hundreds of kelvin both to higher and lower temperatures, depending on the direction of the external field. In addition, the transformation between multi-domain and mono-domain states, induced by an in-plane electric field, results in an additional peak of the adiabatic temperature change at lower temperatures, and a broad temperature interval where the caloric response scales linearly with the applied field strength, even up to very high fields.

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Introduction. – Within a ferroic material, a variation of the ferroic order parameter can be induced through application of the corresponding conjugate field. Depending on the thermal boundary conditions, this results in an isothermal entropy or an adiabatic temperature change. For example, if an externally applied conjugate field is removed under adiabatic conditions, order parameter and temperature typically decrease. It has been shown that “giant” caloric effects occur for different classes of materials in the vicinity of field-induced structural-ferroic transitions [1,2]. For example, in ferroelectric BaTiO$_3$ (BTO), the largest field-induced change of the order parameter (electric polarization, $P$), and thus the largest adiabatic temperature change, is observed for temperatures slightly above the transition between the cubic paraelectric high-temperature phase and the tetragonal ferroelectric phase at about 400 K [3,4]. Systems that exhibit such giant caloric effects have a huge potential for the development of novel cooling concepts [5–7]. For the case of the electro-caloric effect (ECE) [6,8], much work is focused on thin films [2,3,6,8,9], as the magnitude of the ECE generally increases with the strength of the applied electric field [10], and large fields can be induced by moderate voltages within thin films [9]. In addition, the high surface-to-volume ratio allows for a fast heat transfer to the environment and thus, potentially, for fast cycling of a device. Thin films also allow to combine the advantages of single crystals (well-defined crystallographic orientation) and poly-crystals (mechanical stability during cycling).

Furthermore, thin films are often subject to strain, which can strongly affect the ferroelectric properties, and thus provides an efficient way for tailoring the desired functional properties [11]. If a material such as BTO is grown epitaxially on a surface representing a square lattice, a biaxial strain, $\eta$, is imposed along the two in-plane directions ($a$ and $b$), whereas the lattice constant along the film normal ($c$) can adjust freely. As a result, the ferroelectric transition temperatures and the relative stability of different ferroelectric phases of BTO are modified, as depicted in fig. 1 [12–17]. For zero strain, i.e. pure clamping by the substrate, both in-plane and out-of-plane components of the polarization appear at the same transition temperature $T_C$, equal to the bulk transition temperature. Tensile (positive) strain then increases the transition temperature for the in-plane components (along $a$ and/or $b$) and decreases the transition temperature for the out-of-plane component (along $c$), and vice versa for compressive strain [12,15]. In addition to the ferroelectric mono-domain phases found at low temperatures, multi-domain configurations are stabilized between $T_C$ and $T_S$ [14,16–19].

Generally, a field-induced change of polarization and a resulting adiabatic temperature change occur for all values of strain and all temperatures. However, the largest effect...
Fig. 1: (Color online) Schematic phase diagram of BaTiO$_3$ under epitaxial strain, adapted from [17]. Colors encode different polarization ($P$) directions (also illustrated by the insets). Red: $P$ along $c$; light blue: $a/b$ multi-domain state ($P$ as sketched on the upper right-hand side); darker blue: $ab$ mono-domain state ($P$ as sketched on the lower right-hand side); light purple: $ac/bc$ domains (in-plane $P$ as for $a/b$ domains with homogenous $P$ along $c$); darker purple: $abc$ mono-domain phase. White dotted lines border multi-domain phases. $T_C$ ($T_S$) indicates the strain-dependent transition temperature for in-plane $P$ (for the multi-domain to mono-domain transition). The grey area below the bulk $T_C$ for $\eta \approx 0$ indicates a region with complex multi-domain states.

is usually observed just above $T_C$. This can be understood from the following relation (cf. ref. [6]):

$$\Delta T = -\int_{E_1}^{E_2} \frac{T}{C_E(T,E)} \frac{\partial P}{\partial T} \, dE.$$  

(1)

Here, the electric field $E$ is varied from $E_1$ to $E_2$ under adiabatic conditions, $P$ is the polarization component along the field direction, and $C_E$ is the specific heat at constant field (and constant pressure). The largest changes, $\partial P/\partial T < 0$, occur just above $T_C$ (where the field causes a transition or crossover to the ferroelectric phase), resulting in a strong peak of $\Delta T(T)$ with a relatively sharp drop on the low-temperature side and a broad shoulder towards higher temperatures, see, e.g., refs. [2,6].

Most previous studies investigating the influence of epitaxial strain on the ECE in BTO have concentrated on compressive strain [20–23]. In contrast, the influence of tensile strain has so far only been investigated based on phenomenological models, with partly contradicting results. For example, both an increasing [20] and a decreasing [21,22] maximal-temperature change have been reported. Such discrepancies, which can be caused by different model assumptions or parameterizations, can be resolved through ab-initio–based simulations. Furthermore, for both kinds of strain we are only aware of investigations on the role of an electric field along the surface normal. However, the ECE in single crystals can depend strongly on the direction of the applied field [24–26]. In addition, the ECE in the multi-domain states with $a/b$ and $ac/bc$ domains and, in particular, at the corresponding multi-domain to mono-domain transitions at $T_S$, has not been investigated so far.

In this paper, we address the following questions: Does tensile strain enable or hamper a large caloric response? In particular, can such strain help to obtain a significant ECE over a broad temperature range around ambient temperatures, which is desirable for many applications? How does the strain-induced multi-domain state affect the ECE? To understand these issues, we explore the role of tensile strain on the caloric response of BTO, using ab-initio–based simulations and taking different directions of the applied field into account. We show that tensile strain $\leq 1\%$ can be used to shift $T_{\text{max}}$ by several hundreds of kelvin both to higher and lower temperatures, depending on the direction of the external field. In addition, the transformation between multi-domain and mono-domain states, induced by an in-plane electric field, results in an additional peak of $\Delta T(T)$ at lower temperatures, and a broad temperature interval where the caloric response scales linearly with the applied field strength, even up to very high fields.

**Methods.**–Molecular-dynamics simulations are performed, employing an effective Hamiltonian [27] as implemented in the FERAM code developed by Nishimatsu et al. [28]. The ab-initio–based parametrization of the effective Hamiltonian for BTO is taken from ref. [29]. Periodic boundary conditions and a cell size of $96 \times 96 \times 96$ BTO units have been used. We model the epitaxial strain imposed through a hypothetical substrate by fixing the elements $\eta_1 (\equiv \eta_a)$ and $\eta_2 (\equiv \eta_b)$ of the homogenous strain tensor (in standard Voigt notation) to the external strain $\eta$ and setting $\eta_c = 0$. We define zero strain for a lattice constant of 3.996 Å, which we obtain for the paraelectric phase of bulk BTO directly above $T_C$.

We note that, due to the large size of our simulation cell, we obtain additional domain configurations, with local polarization along various crystallographic directions, for very small strain values ($|\eta| < 0.1\%$) directly below $T_C$ (see grey area in fig. 1). These configurations are absent for the smaller simulation cell used in ref. [17]. Since these additional domain configurations appear only in a very limited region within the phase diagram they are not relevant in the context of the present study and are therefore not discussed any further.

The caloric response is obtained from the following protocol: I) We start our simulations above $T_C$ and equilibrate the system within an external field. Afterwards, we reduce the temperature in steps of maximal 10 K, using the final configuration from the previous temperature step as initial configuration, i.e., we field-cool the system. These simulations are performed in the NPT ensemble using a Nosé–Poincaré thermostat and a time step of $\Delta t = 2$ fs [30]. II) At each measuring temperature we start from the corresponding field-cooled configuration,
switch to the micro-canonical ($NPE$) ensemble and perform direct simulations of the ECE. Advantages and technical details of this method are discussed in refs. [31–33]. We ramp down the field with the rate of 0.002 kV/cm/fs. This ramping rate is sufficiently slow to ensure thermodynamic equilibrium except very close to the ferroelectric phase transition, where the dynamic of the system slows down considerably. We thus use further equilibration of at least 40 ps previous to measuring the adiabatic temperature change.

We note that the simplifications necessary to construct the effective Hamiltonian lead to quantitative deviations of the calculated ferroelectric transition temperatures ($T_c$) compared to experiment [27,29]. Nevertheless, qualitative trends and the overall magnitude of polarization and strain are well described and are generally in good agreement with experimental observations, cf. refs. [15,17]. Furthermore, only 3 out of 15 degrees of freedom per BTO unit are explicitly taken into account in our simulations, resulting in a reduced specific heat, and thus an overestimated temperature change $\Delta T$. In the following, we therefore rescale the calculated $\Delta T$ by a factor of 1/5, according to the ratio between the considered and total number of degrees of freedom, cf. refs. [32,34].

**Results.** – Figure 2 shows the calculated electro-caloric temperature change as function of the initial temperature under removal of an electric field of 100 kV/cm applied along the out-of-plane and in-plane directions for different amounts of tensile strain.

We first discuss the case of zero applied strain, $\eta = 0$, i.e., pure clamping, for both field directions. As already discussed in refs. [20,23] clamping reduces the ECE and results in a broadening of the $\Delta T$-peak. For the field along the surface normal we find a reduction by a factor of two compared to the free bulk system (from about 4 to 2 K for an external field of 100 kV/cm) and the full width at half-maximum (FWHM) increases from about 35 K (unclamped) to about 55 K (clamped). If the field is applied along the in-plane $ab$-direction, the peak value of the ECE, $\Delta T(T_{max})$, is reduced to about 1.7 K at $T_{max} = 290$ K, while the FWHM increases to about 70 K. Thus, in spite of the reduction compared to the free bulk case, a large ECE is still obtained for the clamped system for both field directions.

We note that we find small temperature and field regions where $\partial P/\partial T|_E > 0$, e.g., at the transition temperatures of the ferroelectric phase polarized perpendicular to the external field. As a consequence, the adiabatic temperature in these temperature regions is reduced and even an inverse ECE, i.e., a heating of the system under field removal occurs, cf. eq. (1). For instance, at the transition temperature of the in-plane polarization, $T_c \approx 270$ K, for field along $c$, $\Delta T$ changes its sign. In addition, an inverse ($\Delta T > 0$) peak exists around $T \approx 190$ K, the transition temperature to a different multi-domain configuration observed for $\eta \approx 0$. The magnitude of these inverse peaks may be underestimated due to the used temperature grid and as several (meta-)stable domain configurations seem to coexist.

Focusing next on the strain dependence of $\Delta T(T)$, depicted in fig. 2, one can observe that increasing tensile strain shifts the position of the peak in $\Delta T$, $T_{max}$, towards higher (lower) temperatures if the electric field is applied in-plane (out-of-plane). Thus, the peak positions essentially follow the transition lines (II) and (III) in fig. 1 for the appearance of spontaneous polarization along the respective field direction. Furthermore, with decreasing (increasing) $T_{max}$, the FWHM of the ECE peak increases (decreases). For example, for a field along $c$ the FWHM increases approximately linearly with strain from about 55 K to about 90 K between 0 and 0.45% while the FWHM for a field along $ab$ is about 50 K for 0.25–0.45% and is reduced to 40 K for 0.75% strain.

Most strikingly, the maximum of the ECE, $|\Delta T(T_{max})|$, increases (decreases) systematically, if the corresponding peak position is shifted to higher (lower) temperatures. This relationship between $|\Delta T(T_{max})|$ and $T_{max}$ for different strains can be understood from eq. (1). Even though all quantities under the integral in eq. (1) depend on
temperature (and, of course, on the electric field), we find that the change of the peak value of $\Delta T$ under strain is dominated by the explicit factor $T$ in the integrand. This is analogous to what has been found in ref. [23] for BTO under compressive strain and electric field along $c$, see the corresponding transition line (I) in fig. 1, using the same microscopic model as used in the present work.

The same trend, i.e. increasing $|\Delta T(T_{\text{max}})|$ with increasing $T_{\text{max}}$, due to the strain-induced shift in the ferroelectric transition temperature, has also been found in [21] using a modified transverse Ising model and in [22] using phenomenological Landau theory. In contrast, ref. [20], also using Landau theory, has reported the opposite trend, namely decreasing $|\Delta T(T_{\text{max}})|$ with increasing $T_{\text{max}}$ (and thus increasing $|\Delta T(T_{\text{max}})|$ under increasing tensile strain). The increase of $|\Delta T|$ found in ref. [20] was attributed to a stronger first-order character, and thus increasing $\partial P/\partial T|_E$, under tensile strain, cf. eq. (1). This can be confirmed neither by our ab-initio-based microscopic model nor by the phenomenological models used in [21,22]. We note that, while the Landau free energy in [20] is expanded up to the sixth order in the polarization, with temperature-dependent second- and fourth-order coefficients, ref. [22] uses a different parameterization based on an eighth-order expansion with a temperature-independent fourth-order coefficient.

In addition to the main peak at $T_{\text{max}}$, corresponding to the ferroelectric transition temperature of the polarization component along the field direction, for small values of tensile strain and field along $c$ we also observe a small feature in $\Delta T$ at the in-plane transition temperature $T_{C_{a/b}} > 300$ K. Here, the onset of the in-plane polarization results in a reduced magnitude (or even reversed sign) of $\Delta T$, related to regions with negative $\partial P/\partial T|_E$. We note that this is analogous to the “double-peak structure” reported in [22] for tensile strains smaller than 0.15%. With increasing strain, the magnitude of the “peak” at higher temperatures decreases as $T_{C_{a}}$ and $T_{C_{b}}$ move apart, see fig. 1.

Summarizing the results presented so far, we point out that epitaxial strain can be used to systematically increase or decrease the temperature range with large ECE over several hundreds of kelvin for rather moderate strain values of less than 1%, depending also on the direction of the applied field. In fact, for many of the anticipated device applications, it is important to reduce $T_{\text{max}}$ to ambient temperatures (and also to obtain a sufficiently large $\Delta T$ over a broad temperature interval around $T_{\text{max}}$). Here, we find $T_{\text{max}}$ about 100 K below the bulk $T_C$, and thus in a very attractive temperature range for applications, for only 0.25% tensile strain (see fig. 2(a)).

Next, we discuss the ECE for the multi-domain state observed under tensile strain in the temperature range between $T_C$ and $T_S$. As can be seen in fig. 2(b) for an electric field applied along $ab$, a second peak in $\Delta T(T)$ is found near the strain-dependent transition temperature $T_S$, indicated as (IV) in fig. 2. The appearance of this peak can be explained as follows. Below $T_S$, the system is in a mono-domain state with a large polarization that depends only weakly on temperature and field. Consequently, the system exhibits only a very weak ECE below $T_S$. If an external field along $ab$ is applied, $T_S$ shifts to higher temperatures, e.g., for 0.75% strain, $T_S$ increases from 185 K (no field) to 220 K (100 kV/cm) to 370 K (500 kV/cm). Therefore, if the external field is increased starting from an initial temperature slightly above $T_S$, the system transforms reversely from a multi-domain to a mono-domain state. Since the net polarization along $ab$ in the multi-domain $a/b$ state is smaller than in the mono-domain $ab$ phase, the polarization is strongly field- and temperature dependent around this transition, resulting in a pronounced peak in $\Delta T$.

While for $\eta = 0$ the corresponding peak value $\Delta T(T_{C_{a/b}}^{\text{S}})$ for an external field of 100 kV/cm is less than 0.5 K, $\Delta T(T_{C_{a/b}}^{\text{S}})$ increases with increasing tensile strain and becomes larger than 1 K for 0.75% strain at about 75 K below the zero-strain $T_C$, see fig. 2(b). This increase of $\Delta T(T_{C_{a/b}}^{\text{S}})$ is again related to the corresponding increase of $T_{C_{a/b}}^{\text{S}}$ via eq. (1), as discussed above for the main ECE peak.

Apart from the additional peak in $\Delta T$, we also observe a moderately large ECE (~0.5 K for 0.75% strain) within a rather broad temperature interval between the two main ECE peaks, namely in the temperature range between $T_S$ and $T_C$ corresponding to the strain-induced multi-domain configuration. While the corresponding $\Delta T$ is small compared to the peak values, it is noticeably larger than within the ferroelectric mono-domain phase below $T_S$. This enhanced ECE is due to the field-induced (and temperature-dependent) gradual rotation of the local polarization from $a/b$ towards $ab$. Furthermore, as we show in the following, the ECE in this multi-domain region can be considerably enhanced by increasing the field strength.

Figure 3 shows the “electro-caloric strength”, defined as $\Delta T/\Delta E$ [2], both under compressive and tensile strain for different applied fields. It can be seen that in both cases the electro-caloric strength decreases near $T_{\text{max}}$ while it increases for even higher temperatures as the field increases. For lower temperatures, which are most relevant for practical cooling applications, the electro-caloric strength under compressive strain is very small and decreases further with the field strength. In contrast, the electro-caloric strength under tensile strain is approximately constant between $T_C$ and $T_S$, around $-0.004 \text{ K} \cdot \text{cm}/\text{kV}$, even for field strengths up to 500 kV/cm. Thus, between $T_C$ and $T_S$ the ECE grows linearly with the field, and already for a field strength of 200 kV/cm an adiabatic response of 1 K can be obtained in a very broad temperature interval below $T_C$. For 0.75% strain, this large and broad response occurs about 100 K below the bulk $T_C$, i.e., corresponding to ambient temperatures.

Up to now, the in-plane electric field in our calculations was always oriented along the $ab$-direction. However, we note that even for a misaligned field, a rather strong ECE near $T_S$ is obtained. For example, for an in-plane field...
along \( a \), we find a similar \( \Delta T(T) \) profile and a similar ECE peak at \( T_S \) as for the case with the field along \( ab \), see fig. 4. Only the magnitude of the ECE between \( T_C \) and \( T_S \) and close to the peak at \( T_C \) are reduced. This reduced \( \Delta T \) for \( E \) along \( a \) is most likely due to the polarization-strain coupling, which does not allow the polarization to rotate fully into the field direction, due to the epitaxial constraint.

Finally, we note that we use “poled” (field-cooled) starting configurations in our simulations, and, therefore, our results do not include irreversible contributions which can arise in the first field cycle, depending on the thermal history and field treatment of the samples. This can occur due to the existence of different meta-stable multi-domain states, specifically for fields applied along \( a \) and \( \eta \rightarrow 0 \).

Conclusions and outlook. – In summary, we have investigated the effect of epitaxial strain on the caloric response of BTO through \textit{ab-initio}–based molecular-dynamics simulations. We have focused on tensile strain, which provides a very promising route to enhance the ECE at room temperature and below. With increasing tensile strain, the ECE is systematically reduced for fields along the surface normal. However, since the optimal operation temperature is shifted towards ambient temperatures, small values of tensile strain can be useful in order to optimize the ECE at ambient temperatures. In addition, the

ECE peak broadens with increasing tensile strain, which is also favorable for applications.

For an electrical field applied within the surface plane, the ECE exhibits two peaks, one slightly above the ferroelectric transition temperature, \( T_C \), and one close to the transition temperature \( T_S \) between the mono-domain and multi-domain ferroelectric phases. Although, the latter is smaller than the peak at \( T_C \), it occurs in a temperature range that is very attractive for many applications. Furthermore, \( T_S \) can be adjusted with the magnitude of the strain. Between the strain-dependent temperatures \( T_S \) and \( T_C \), we find a reversible coupling between external field and the domain configuration. This strong coupling allows for a linear increase of the ECE with the strength of the external field, and thus large adiabatic temperature changes can be obtained within a broad temperature range. Thus, tensile epitaxial strain can be used to enhance the caloric response of BTO well below the ferroelectric transition temperature, and a considerable ECE around and below room temperature can be achieved if the external electrical field is applied within the surface plane.

Recently, it has been pointed out that the electric-field control of the domain structure in BTO can improve the caloric response of FeRh films grown on BTO [35]. Our results suggest that the caloric response of the BTO domain structure itself should also be taken into account, and that the resulting multicaloric properties can be further optimized through epitaxial strain. In the same spirit, one could also consider to use piezoelectric, magnetostrictive, or mechanically bendable substrates to adjust the caloric response of BTO by shifting its optimal operation range to higher and lower temperatures, which then allows to adjust the cooling device to a specific heat source.

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