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Influence of Stress on the Chiral Polarization and Elastocaloric Effect in BaTiO₃ with 180° Domain Structure

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Abstract: The polarization and elastocaloric effect of chiral barium titanate (BaTiO₃) with an Ising–Bloch-type domain wall under stress was investigated using the Landau–Ginzburg–Devonshire (LGD) theory. It has been shown that tensile stresses increase the magnitude of the Ising polarization component in barium titanate, together with a decrease in the domain wall width. Compressive stresses cause a reduction in the Ising polarization component and an increase in the domain width. Under compressive stress, barium titanate exhibits a negative elastocaloric effect and temperature changes with increasing stress, while BaTiO₃ exhibits a positive elastocaloric effect under tensile stress. Bloch polarization shows angle-dependent polarization under external force, but the temperature change from the elastocaloric effect is smaller than that of Ising polarization under stress. This work contributes to the understanding of polarization evolution under tension in ferroelectrics with chiral structure.

Keywords: chiral polarization; elastocaloric effect; domain structure



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1. Introduction

Ferroelectric materials are generating significant interest for their potential use in devices that rely on the combination of spontaneous polarization that can be altered by an external electric field or stress [1–4]. Ferroelectric devices consist of ferroelectrics with a domain structure characterized by varying polarization orientations [5,6]. The domain walls in ferroelectrics, which are an important part of the domain and have a large influence on the properties of ferroelectric materials [7,8], have been investigated extensively by various methods, including atomic force microscopy [9], X-ray diffraction methods [10,11], and X-ray diffractometry [12,13]. A single domain wall can be considered to be a viable unit of information in nano-electronic devices, aligning with the ongoing trend of shrinking electronic devices [14–16]. Conventionally, the 180° domain walls in ferroelectrics are regarded as Ising-type, wherein the magnitude of the polarization component alters but does not rotate along the domain walls [17–19]. In the field of early thermodynamics, Lajzerwicz and Niez made a prediction that the order parameter present in the domain wall is specifically chirality [20]. The presence of a Néel or Bloch-type domain wall in ferroelectrics has been demonstrated using density functional theory calculations, Landau–Ginzburg–Devonshire (LGD) calculations and phase field simulations [21–27]. In experiments, the Néel-type domain wall was observed in the ferroelectric crystals of Pb(Zr_{1–x}Ti_x)O₃ using transmission electron microscopy [28]. Using nonlinear optical microscopy, a dominant Bloch-like form in the trigonal LiTaO₃ bulk crystal was reported [29]. The chiral textures of domain walls in ferroelectric antiferromagnet BiFeO₃ were observed using reciprocal and real-space characterization techniques [30]. Epitaxial lead titanate thin films were used to illustrate the presence of 180°-domain walls with non-Ising polarization at ambient temperatures [31]. To utilize chiral polarization in electrical devices, it is necessary to investigate its behavior

under various external fields. It has been demonstrated that chirality in ferroelectric materials can be tuned using a variety of methods. The electric field can be used to regulate and switch the ferroelectric thin film and nanodots of PbTiO_3 , which exhibit the chirality of skyrmions [32,33]. The achiral domain wall, a characteristic feature of the Bloch-type domain wall, has garnered significant attention [34]. The polarization component within the achiral structure exhibits opposite rotational orientations on both sides of the domain walls, with its center crossing the zero point. In contrast to the classical Bloch-domain wall, the achiral structure maintains the symmetry of the wall, reduces the domain energy and enhances the stability of its features [35,36]. The presence of an achiral domain wall has been discovered to significantly affect the mobility of the domain wall in a PbTiO_3 thin film [37], as well as the electrocaloric effect in BaTiO_3 [38]. Extensive research has been conducted on the study of the caloric impact in ferroelectric materials, specifically focusing on the electrocaloric and elastocaloric effects. Those works are motivated by the possible use of these phenomena in solid-state refrigeration [39–42]. However, the detection of the Bloch polarization component in chiral ferroelectric materials presents a difficult task in experiments, leading to a restricted investigation of chiral polarization in the caloric effect of ferroelectric materials. Hence, it is crucial to examine the influence of chiral polarization on the caloric effect from a theoretical standpoint. Nevertheless, the impact of the achiral structure on the elastocaloric effect in ferroelectrics remains unexplored.

In this work, a theory was established to investigate the influence of stress on polarization and the elastocaloric effect based on the Landau–Ginzburg–Devonshire (LGD) theory. With the Bloch components, flexoelectricity is introduced into the LGD theory. The magnitude of the Ising and Bloch polarization components of BaTiO_3 (BTO) with a 180° domain wall was investigated in detail. The elastocaloric adiabatic temperature change under stress with different polarization components was calculated.

2. Materials and Methods

Tetragonal BTO, a typical ferroelectric material, was chosen because there is evidence for the existence of Ising–Bloch–Néel-type components. [26]. According to Figure 1a, the Ising-type component (P_1) is defined as the component parallel to the spontaneous polarization $\pm P_s$. The Bloch-type component (P_2) is perpendicular to the Ising-type component but parallel to the plane of the domain wall. The Néel-type component (P_3) is smaller than the Bloch-type component and is not considered in this work. It is expected that flexoelectricity may produce Bloch- and Néel-type components in tetragonal BTO. The Gibbs free energy (G) of BTO with a 180° domain is described as follows

$$G = A_{ij}P_iP_j + B_{ijkl}P_iP_jP_kP_l + C_{ijklmn}P_iP_jP_kP_lP_mP_n + \frac{1}{2}D_{ijkl}\frac{dP_i}{dx_j}\frac{dP_k}{dx_l} \quad (1)$$

$$- Q_{ijkl}\sigma_{ij}P_kP_l - \frac{1}{2}s_{ijkl}\sigma_{ij}\sigma_{kl} - \frac{1}{2}F_{ijkl}\left(\sigma_{ij}\frac{dP_k}{dx_l} - P_k\frac{d\sigma_{ij}}{dx_l}\right) - P_i\left(E_i + \frac{E_i^d}{2}\right)$$

where $E_i = -\partial\varphi/\partial x_i$ is an electric field, A_{ij} , B_{ijkl} and C_{ijkl} are dielectric stiffness coefficients, D_{ijkl} is the gradient energy coefficients, Q_{ijkl} is the electrostriction strain tensor, s_{ijkl} is the elastic compliances, σ_{ij} is the stress tensor components, F_{ijkl} is the flexoelectric coupling energy, and E_i is the applied electric field. $E_i^d = -P_3/(\epsilon_0\epsilon_b)$ is considered, where ϵ_0 denotes the dielectric constant of the vacuum. As seen in Figure 1, the orientation of the wall between the normal and the cubic crystallographic direction is θ . This is a crystallographic cubic reference (x_{c1} , x_{c2} , x_{c3}) to characterize the domain tilt.

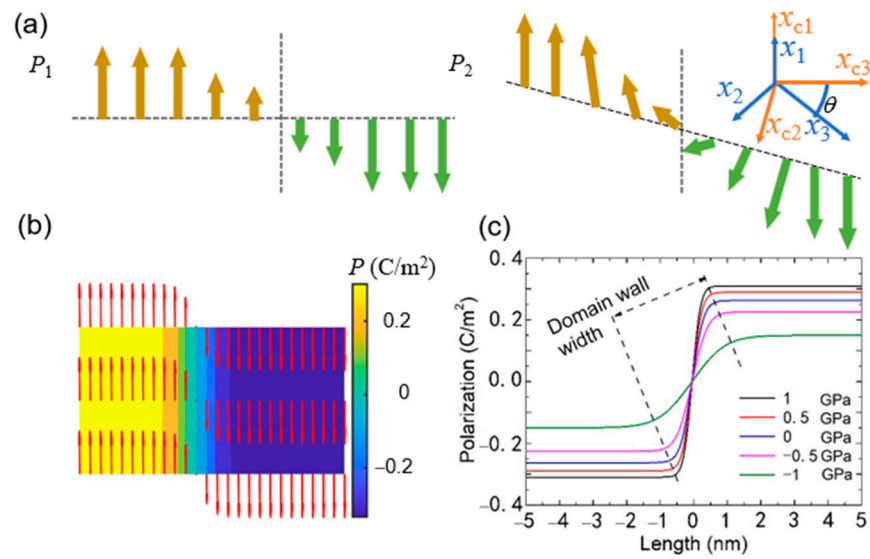


Figure 1. (a) Schematic representation of the polarized components of the Ising and Bloch type; (b) Ising type of the polarized components as a function of position in BaTiO₃ at room temperature. (c) Relationship between Ising polarized component and tensile and compressive stresses at room temperature.

For simplicity, we have assumed P_1 and P_2 represent the polarization of Ising walls and Bloch walls with a bichiral structure. In the new reference frame, the polarization components have the form of,

$$2a_1P_1 + 4a_{11}P_1^3 + 2a_{12}P_2^2P_1 + 6a_{111}P_1^5 + 4a_{122}(\alpha)P_1P_2^4 - D_{66}\frac{\partial^2 P_1}{\partial x_3^2} - 2(Q_{11}\sigma_1 + Q_{12}\sigma_2)P_1 - Q_{66}\sigma_6P_2 - \frac{\partial \varphi_1}{\partial x_3} = 0 \quad (2a)$$

$$2a_1P_2 + 4a_{22}P_2^3 + 2a_{12}P_1^2P_2 + 6a_{222}P_2^5 + 2a_{112}P_1^4P_2 + 4a_{122}P_1^2P_2^3 - D_{44}\frac{\partial^2 P_2}{\partial x_3^2} - 2(Q_{22}\sigma_2 + Q_{12}\sigma_1)P_2 - Q_{66}\sigma_6P_1 - F_{24}\frac{\partial \varphi_2}{\partial x_3} = 0 \quad (2b)$$

The boundary conditions for the polarization and the potential away from walls are

$$P_1(x_3 \rightarrow -\infty) = -P_s, \quad P_1(x_3 \rightarrow \infty) = P_s, \quad P_2(x_3 \rightarrow \pm\infty) = 0, \quad (3a)$$

$$\varphi_1(x_3 \rightarrow \pm\infty) = 0, \quad \varphi_2(x_3 \rightarrow \pm\infty) = 0. \quad (3b)$$

In this paper, relevant parameter needs to be rewritten because of stress, and the designations are used in previous work [16,43]. The elastic stresses are

$$\sigma_1 = \frac{-F_{24}(\alpha)s_{12}(\partial P_2/\partial x_3) + (P_s^2 - P_1^2)(Q_{11}s_{22}(\alpha) - Q_{12}s_{12}) + P_2^2(Q_{22}(\alpha)s_{12} - Q_{12}s_{22}(\alpha)) + (s_{22}F_{12} - s_{12}F_{12})(\partial P_3/\partial x_3)}{s_{22}(\alpha)s_{11} - s_{12}^2} \quad (4a)$$

$$\sigma_2 = \frac{F_{24}(\alpha)s_{11}(\partial P_2/\partial x_3) + (P_s^2 - P_1^2)(Q_{12}s_{11} - Q_{11}s_{12}) + P_2^2(Q_{12}s_{12} - Q_{22}(\alpha)s_{11}) + (s_{22}F_{12} - s_{12}F_{12})(\partial P_3/\partial x_3)}{s_{22}(\alpha)s_{11} - s_{12}^2} \quad (4b)$$

$$\sigma_6 = -\frac{Q_{66}}{s_{66}}P_1P_2 \quad (4c)$$

After the polarization is obtained, the adiabatic temperature change (ΔT) of the BTO under stress is defined as

$$\Delta T = -\frac{T}{C} \int_{\sigma_1}^{\sigma_2} \left(\frac{\partial u}{\partial T} \right)_{\sigma, E} d\sigma \quad (5)$$

where C is the heat capacity, u is the strain, and σ stands for the applied stress. According to the Maxwell relation $\left(\frac{\partial u}{\partial T} \right)_{\sigma, E} = \left(\frac{\partial S}{\partial \sigma} \right)_{E, T}$, the adiabatic temperature change can be derived from the entropy change under the applied stress. For ferroelectrics, the entropy change is given by $\Delta S = [P_\sigma^2(T) - P_0^2(T)] / 2\epsilon_0 C$. Then, the adiabatic temperature change in ferroelectrics can be determined as an expression of the polarization change. The parameter used in this work can be found in the literature [17,39,40].

3. Results and Discussion

We first obtained the 180° domain structure of barium titanate without applied stress, which can be seen in Figure 1b. This 2D diagram was reconstructed using three 1D polarization maps determined by calculation, with the individual 1D polarizations shown in the red dashed box in the figure. It can be seen that the domain wall width of this 180° domain is about 2 nm and the magnitude of its polarization is 0.26 C/m^2 , which is consistent with the experimental observations [44]. The stress exerted along the thickness of the barium titanate is investigated. The evolution of the Ising polarization component of barium titanate under tensile and compressive stress is shown in Figure 1c. At a tensile stress of 1 GPa, the Ising polarization component of 0.31 C/m^2 is larger than that without tensile stress (0.26 C/m^2), while the polarization component decreases to 0.15 C/m^2 at -1 GPa . This is due to the fact that tensile stress increases the lattice constant along the c -axis in the barium titanate, which leads to an increase in the potential shift and thus the polarization. In contrast, compressive stress decreases the lattice constant and leads to a decrease in polarization [45]. Figure 1c also shows the variation in domain widths under different stresses. Compressive stress leads to an increase in domain wall width, while tensile stress leads to a decrease in domain wall width.

Then, the effect of the elastocaloric temperature change (ΔT) caused by the change in the Ising polarization of barium titanate under external stress was studied. For the simulation, the applied external force is gradually increased from 0.1 GPa to 1 GPa. Figure 2a shows the temperature change in barium titanate under compressive stress, whereby barium titanate exhibits a negative elastocaloric effect. When the compressive stress increases from -0.1 to -1 GPa , the minimum adiabatic temperature change decreases from -0.14 K to -2.3 K . According to Equation (5), the magnitude and sign of the adiabatic temperature change are related to the magnitude of the polarization before and after the applied stress. The compressive stress leads to a decrease in polarization, which results in a negative adiabatic temperature change. In contrast, tensile stress leads to an increase in polarization so that a positive elastocaloric effect occurs under tensile stress, see Figure 2b. Both Figure 2a,b show that the temperature change at the domain wall is larger than that of the ferroelectric domains. This is due to the fact that the temperature change at the domain wall is larger and the value of the polarization change caused by the external force is larger, resulting in the larger temperature change. Notably, the polarization at the domain wall does not change, so there is no temperature change. The comparison between the mean value of (ΔT_{mean}) and maximum (ΔT_{max}) or minimum (ΔT_{min}) adiabatic temperature change in BTO under the tension and compression as a function of stress is shown in Figure 2c,d. When the compressive stress decreases from -0.1 to -1 GPa , ΔT_{min} decreases from -0.17 to -2.34 K , as shown in Figure 2c. Figure 2d shows that the ΔT_{max} of BTO increases from 0.13 to 1.45 K when then tension increases from 0.1 to 1 GPa . Therefore, the adiabatic temperature change in the ferroelectric material can be enhanced by moving the domain wall since the temperature change caused by the domain wall is much larger than that of the domain.

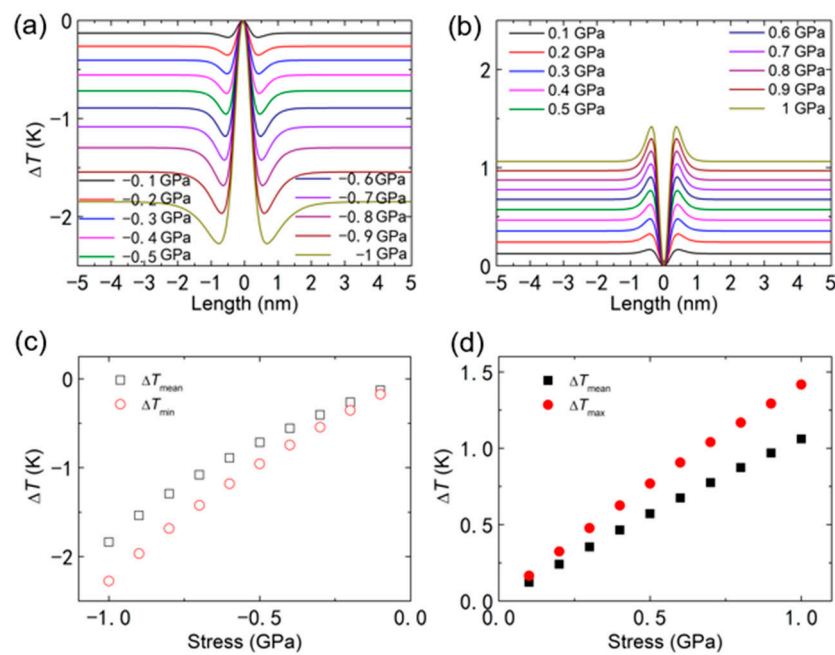


Figure 2. Temperature variation in Ising polarization components in BaTiO₃ under (a) compressive and (b) tensile stresses. The average (ΔT_{mean}), maximum (ΔT_{max}) and minimum (ΔT_{min}) value of BaTiO₃ as a function of (c) compressive and (d) tensile stresses.

The polarization component of domain walls varies with the angle of rotation due to the dependence of flexoelectric coefficients on the rotation of the domain wall. The Bloch components of the BTO are investigated as a function of the angle under different stress conditions, as shown in Figure 3a. Figure 3a shows that the Bloch polarization component (0.02 C/m²) is much smaller than the Ising polarization component (0.26 C/m²). The magnitude of the P_2 component in the BTO without tension or compression is zero $\theta = n\pi/4$, where n is an integer. When the angle rises to $\pi/12$, the magnitude of P_2 achieves its greatest value and subsequently declines to zero when the angle increases to $\pi/4$. The P_2 polarization rises in magnitude under the application of compressive stress. Figure 3b shows the Bloch polarization of BTO, which is shown as a green dashed line in Figure 3a. P_2 increases from 0.02 C/m² at -0.1 GPa to 0.05 at -1 GPa. The P_2 polarization decreases from 0.024 to 0.019 C/m² under the tensile stress. The tensile stress leads to a reduction in Bloch polarization, and the compressive stress increases it. This can be explained by the decrease in polarization caused by the tensile stress, which reduces the lattice constant. On the contrary, the Bloch polarization increases under compressive stress as the lattice constant increases along the x -axis.

The presence of the Bloch component P_2 leads to an additional polarization near the domain wall that can affect the ΔT of BTO. The contribution of the Bloch-type polarization component on the ΔT in the BTO is illustrated in Figure 4a,b. Under tensile stress, Bloch polarization of the barium titanate exhibits a negative elastocaloric effect, and the absolute value of temperature change increases with the increase in tensile stress. This is a decrease in polarization due to tensile stress. According to Equation (5), Bloch polarization shows a positive elastocaloric effect under compressive stress. ΔT increases with the increase in compressive stress and reaches a maximum value of 0.015 K at 1 GPa. At 1 GPa, ΔT reaches -0.001 K. However, this temperature change is much smaller than the temperature change caused by Ising polarization. This study shows that the main contribution to the elastocaloric effect in ferroelectric materials is related to the Ising polarization component.

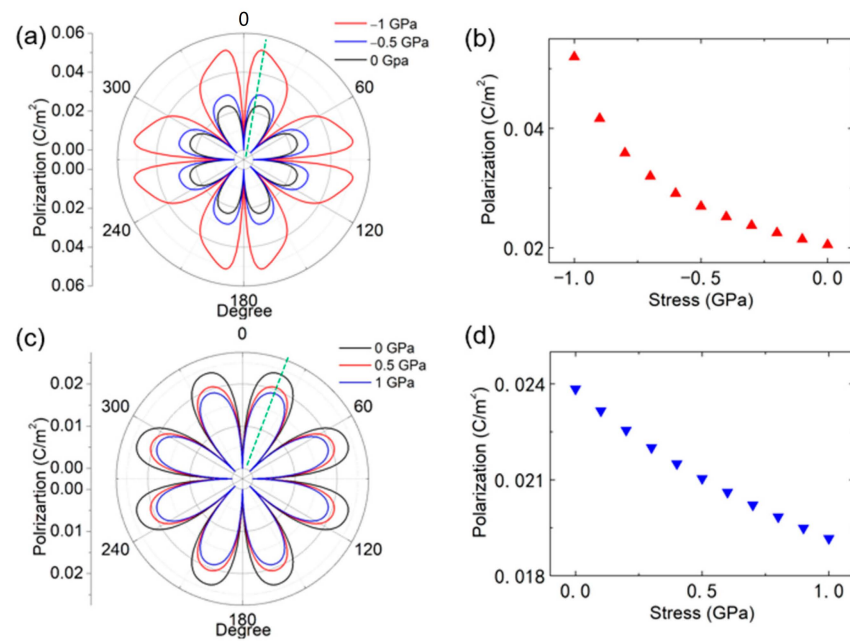


Figure 3. (a) The polarization component of P_2 as a function of rotation angle π in the BaTiO₃ under compression. (b) The magnitude of P_2 at $\pi/24$ as a function of angle. (c) The polarization component of P_2 as a function of the angle of rotation π in the BaTiO₃ under tensile stress. (d) The magnitude of P_2 at $\pi/12$ as a function of angle.

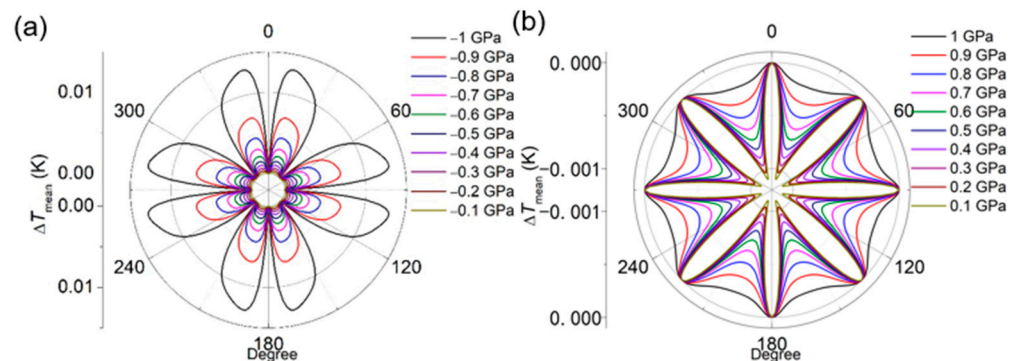


Figure 4. Adiabatic temperature induced by the P_2 polarization component in the BaTiO₃ with the 180° domain wall as a function of angle under (a) compressive stress and (b) tensile stress.

When the temperature decreases, BaTiO₃ would transform from a cubic without polarization to a tetragonal with the polarization along the $\langle 100 \rangle$ direction at 373 K, to an orthorhombic with polarization along the $\langle 110 \rangle$ direction at 278 K, and to a rhombohedral with polarization along the $\langle 111 \rangle$ direction at 183 K. This means that the chirality associated with the polarization does not exist in the cubic. It is believed that this method can be used to study the influence of external stress and electric fields on the chirality of ferroelectric PbTiO₃ since it has the same tetragonal structure as BaTiO₃ at room temperature. For the orthorhombic and rhombohedral, the polarization component would increase with decreasing temperature, which has been studied in many works and therefore is not shown in this work. The 180-degree domains can be considered simplistically as consisting of two single domains with opposite polarization directions. The elastocaloric adiabatic temperature of BaTiO₃ with a single domain structure is plotted as a function of temperature, as shown in Figure 5. The change in adiabatic temperature increases with temperature, reaching a maximum near the Curie temperature and then decreasing rapidly as the temperature continues to rise. Under compressive stress, the negative adiabatic temperature change increases with decreasing temperature. Accordingly, it can be assumed that the

temperature trend of Ising polarization under external stress is similar to that of single domains. However, the temperature change near the domain wall may be different for Ising polarization than for single domains and should be investigated using an appropriate theory. The Bloch-type polarization component may be different due to the change in symmetry and will be investigated in the future.

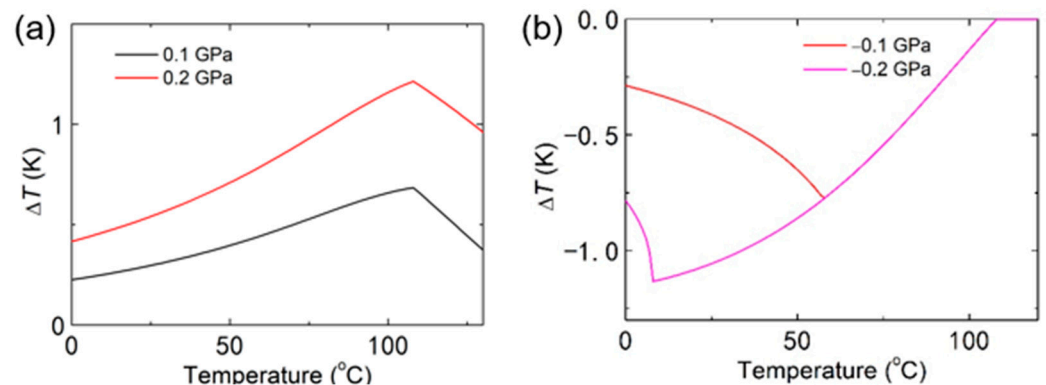


Figure 5. Elastocaloric adiabatic temperature change in BaTiO₃ with single domain structure as a function of temperature, (a) compressive stress and (b) tensile stress.

Barium titanate has both piezoelectric and pyroelectric properties due to symmetry breaking. This means that external forces act on both the piezoelectric and pyroelectric properties of barium titanate with a chiral structure. The piezoelectric coefficient (d_{33}) of the ferroelectric has the form of $d_{33} = 2\varepsilon_{33}\varepsilon_0 \left[Q_{11} - \frac{2s_{11}Q_{12}}{s_{11}+s_{12}} \right] P$, where Q_{11} and Q_{12} are the electrostrictive coefficients, S_{11} and S_{12} are the elastic constants, ε_{33} and ε_0 are the dielectric constant and the dielectric constant of the vacuum [46]. Therefore, the chiral Bloch structure contributes to the piezoelectricity of the ferroelectric. Moreover, the pyroelectric and electrocaloric effects are inverse effects, so the trends of the properties of pyroelectric and electrocaloric effects under external forces are similar. Our previous study on the influence of the chirality of barium titanate on the electrocaloric effect shows that Bloch polarization makes a small contribution to the electrocaloric properties. This implies that Bloch polarization also contributes to the pyroelectric effect under an external field. Furthermore, the accuracy of this simulation should be verified experimentally. However, the focus of this work is on the investigation of the influence of stress on the chirality and elastocaloric in BaTiO₃. The corresponding experimental data will be investigated in the future.

4. Conclusions

The Landau–Ginzburg–Devonshire (LGD) theory was used to study the polarization and elastocaloric effect of chiral BTO with an Ising–Bloch-type domain wall under stress. The investigations have shown that the application of compressive stresses reduces the Ising polarization component in barium titanate and increases the domain wall width, while the tensile stresses have opposite effects on the polarization and domain wall width. The BTO shows a negative elastocaloric effect with the application of compressive stresses and a positive elastocaloric effect with tensile stresses that lead to a decrease in temperature. Bloch polarization shows a polarization that varies with angle in response to an external stress, while the temperature change caused by the elastocaloric effect is less significant compared to the temperature change caused by Ising polarization under stress. This study improves our understanding of the polarization and elastocaloric effect occurring in a ferroelectric material with a chiral structure under stress.

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funding acquisition, B.L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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