*Q* – *POP* – *Thermo*: A General-Purpose Thermodynamics Solver for Ferroelectric Materials
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# Abstract:

Q - POP - Thermo is a program designed to compute thermodynamic monodomain equilibrium states and their properties for ferroelectric single crystals and thin films based on the Landau-Ginzburg-Devonshire (LGD) Theory. Utilizing symbolic manipulation with the SymPy Library, the governing equations along with appropriate boundary conditions are solved for speedy minimization of the free energy of a crystal. Utilizing the popular Differential Evolution algorithm, with appropriate hybridization, multiple phase diagrams, such as the pressure-temperature phase diagram for bulk single crystals and the common strain-temperature phase diagram for monodomain thin-film systems can be readily generated. Furthermore, a variety of material properties of stable ferroelectric phases, including dielectric, piezoelectric, and electrocaloric properties, can simultaneously be calculated. Validation studies are presented for both thin-film and single crystal systems to test the effectiveness and capability of the open-source program.

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**Program Summary:** 

**Program Title:** *Q* – *POP* – *Thermo* 

Licensing Provisions: MIT

Programming Language: Python

No. of Lines in Distributed Program: 1,122 lines

No. of Bytes in Distributed Program: 50,990 Bytes

Computer: Variable, supports both single-core and parallel processing

**Operating System:** Variable, as long as Python 3.6+ is installed properly

**RAM**: Normal operation uses ~70 MB of RAM, which is well within the operating capabilities of contemporary workstations and laptop computers.

**External Routines/Libraries:** numpy (Version 1.20.3), sympy (Version 1.8), numericaloptimization (available with Q - POP - Thermo), pandas (Version 1.1.3), scipy (Version 1.6.3)

**Nature of Program:** Python-based program to perform energy minimization to determine the stable states and thermodynamic properties of ferroelectric systems.

**Solution Method:** Algebraic manipulation of boundary conditions and governing equations followed by a hybridized and improved *a priori* Differential Evolution solver to calculate equilibrium polar states and material properties.

# Additional Comments including Restrictions and Unusual Features: None

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**Running Time:** Problem dependent, a single domain or material calculation ranges from a few seconds for a given thermodynamic condition to a few hours for large parameter space sweeps on contemporary workstations and laptops.

#### Introduction:

Understanding the thermodynamics and phase transitions of materials has always been of the utmost importance to exploring material physics and to providing guidance for developing advanced functional and structural materials. Ferroic materials in general and ferroelectric materials in particular are one such functional material and have been used extensively for energy conversion and information storage, among others [1–3]. For example, the epitaxial growth of ferroelectric thin films, such as perovskite oxides, requires a careful choice of an appropriate substrate to control the lattice mismatch, as both the ferroelectric properties and emergent properties at the interfaces are sensitively dependent on this misfit strain[4–7]. In these material design processes, a fundamental understanding of the phase stability and a theoretical estimation of the thermodynamic properties as a function of external conditions can be invaluable to avoid the trial-and-error in experiments.

The Landau-Ginzburg-Devonshire (LGD) theory serves as a simple but useful thermodynamic description of ferroelectric materials[8]. A ferroelectric is defined by the presence of a non-zero electrical polarization in the absence of an external electric field. This polarization, known as the spontaneous polarization, can be reoriented by a sufficiently high electric field, a process known as polarization switching. The thermodynamics of such a ferroelectric phase transition and the intrinsic behavior of polarization switching can be described quite well by the LGD theory. In the framework of the LGD theory, the total free energy of a ferroelectric is described by a polynomial expansion with respect to the spontaneous polarization. The equilibrium state of a ferroelectric is therefore fully described by the minimization of such an LGD potential energy with respect to thermodynamic states subjected to appropriate boundary conditions and balance constraints. The

LGD theory has been extensively utilized to model classical, lead-free, and organic ferroelectric materials and thin films, providing a first estimation of the thermodynamic properties of a monodomain system and setting the foundation of much more expensive mesoscale modeling such as phase-field simulations[4,9–17].

However, due to the nonlinearity of the thermodynamic equilibrium equations, it is rarely possible to calculate analytically the minimum energy states and their thermodynamic properties. Existing implementation of the LGD theory to determine equilibrium states are mostly based on non-public homegrown scripts utilizing commercial numerical software such as Matlab, Mathematica, or Maple. Often the minimization techniques available in such software are used as a black-box, providing users with little flexibility in solving their questions. To this end, we have developed and designed an expandable Python-based program, termed Q - POP - Thermo, for determining the equilibrium phases of a monodomain ferroelectric system and calculating a variety of thermodynamic properties, such as dielectric permittivity, piezoelectric tensors, and electrocaloric coefficients, subject to arbitrary external elastic, electric, or thermal conditions. The use of opensource Python code and the accompanying symbolic notation library (SymPy)[18] offers researchers a user-friendly and efficient computational vehicle for understanding and exploring both well-studied and new ferroelectric material systems. Moreover, we implement the symbolic notation and manipulation to solve the thermodynamic system under certain boundary conditions in a very general sense, which could be extended into other ferroic and multiferroic materials with multidomain states as well. Additionally, other functional and structural materials could be studied as well where appropriate thermodynamic descriptions are available.

The paper is organized as follows. In Section 2, the Landau phenomenological description of ferroelectric thermodynamics is described along with the necessary boundary conditions for various material architectures. In Section 3, the numerical optimization method and implementation are described. Several case studies are presented in Section 4 to demonstrate

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the capability of Q - POP - Thermo. The paper concludes in Section 5 with avenues of further research and a final discussion of the implementation of the program.

### **Thermodynamics of Ferroelectrics**

## Governing Equations

We begin with a ferroelectric system where the polarization is assumed to be spatially uniform. The total energy of the system is composed of multiple energy contributions, namely the bulk chemical potential energy density ( $f_{Landau}$ ), elastic energy density ( $f_{Elastic}$ ), and electrostatic energy density ( $f_{Electrostatic}$ ). Therefore, the bulk energy density can be expressed as,

$$f_{Bulk} = f_{Landau} + f_{Elastic} + f_{Electrostatic}.$$
 (1)

Regarding thin film systems, it is important to consider the epitaxial and thermal strains that exist in a film/substate system. Normally, this is considered using the so-called misfit strains  $\varepsilon_{11}^m$ ,  $\varepsilon_{22}^m$ ,  $\varepsilon_{12}^m$  which represent the difference in stress-free lattice parameters of the substrate and the ferroelectric film.

The Legendre transformation is employed to handle the mixed constant strain and constant stress boundary conditions for different tensor components. For example, if  $f_{Bulk}$  is defined in terms of polarization and stress with coefficients determined under constant stress boundary conditions (commonly referred to as the Elastic Gibbs-free energy), the following Legendre Transformation can be employed to obtain the strain condition for all the components.

$$f_{Film} = f_{Bulk} (P_i, \sigma_{ij}) + \sigma_1 \varepsilon_1 + \sigma_2 \varepsilon_2 + \sigma_6 \varepsilon_6$$
<sup>(2)</sup>

where the  $\sigma_n$  and  $\varepsilon_n$  are the stress and strain components in Voigt notation. A similar Legendre transformation can be applied when  $f_{Bulk}$  is defined in terms of polarization and strain with coefficients determined under constant strain boundary conditions (referred to as Helmholtz-free energy).

For perovskite ferroelectric oxides, while the most common crystallographic orientation of epitaxial films is (001), other higher-index orientations may be desirable for achieving a specific set of properties. To allow arbitrary film orientations, we transform the experimental reference frame (denoted here with ' on applicable tensors) to the crystallographic reference frame for both first and second rank tensors, i.e.

$$P'_i = t_{ij}P_j \to P_j = t_{ji}P'_i,\tag{3}$$

$$\sigma'_{ij} = t_{im} t_{jn} \sigma_{mn} \to \sigma_{mn} = t_{mi} t_{nj} \sigma'_{ij}.$$
(4)

Here  $t_{ij}$  is the Euler rotation matrix for transforming the crystal system, the rotation matrix used in Q - POP - Thermo is presented in the Appendix for interested readers.

The bulk energy density is represented as a polynomial of the spontaneous polarization ( $P_i$ ) up to the 8<sup>th</sup> order,

$$f_{Landau} = \alpha_{ij}P_iP_j + \alpha_{ijkl}P_iP_jP_kP_l + \alpha_{ijklmn}P_iP_jP_kP_lP_mP_n + \alpha_{ijklmnop}P_iP_jP_kP_lP_mP_nP_oP_p.$$
(5)

To use this software to the compute the temperature-strain phase diagrams of a system requires a user to supply the thermodynamic model parameters including the ranges of applicable temperatures and strains. A general practice to obtain the coefficients associated with the Landau energy density function is to fit all the coefficients, ( $\alpha_{ij}$ ...) to a combination of polarization properties, dielectric properties, and Curie Temperature from experimental measurements or atomic-scale calculations. An example of such fitting procedure is described in existing literature[10,12,19].

Depending upon the definition of  $f_{Bulk}$  (i.e., either Helmholtz- or Gibbs-free energy) the elastic energy can be described in differing ways. For example, if  $f_{Bulk}$  is described via the Helmholtzfree energy framework the elastic energy reads as,

$$f_{Elastic} = \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - q_{ijkl} \varepsilon_{ij} P_k P_l, \tag{6}$$

whereas if  $f_{Bulk}$  is described via the Gibbs-free energy the elastic energy becomes,

$$f_{Elastic} = -\frac{1}{2} s_{ijkl} \sigma_{ij} \sigma_{kl} - Q_{ijkl} \sigma_{ij} P_k P_l.$$
<sup>(7)</sup>

Here  $c_{ijkl}, s_{ijkl}, \varepsilon_{ij}$ , and  $\sigma_{ij}$  are the elastic stiffness, elastic compliance, strain, and stress tensors and Einstein summation is assumed. It should be noted here that the elastic compliance and elastic stiffness are measured under constant electric field. The electrostrictive tensors,  $q_{ijkl}$  and  $Q_{ijkl}$ , are related via,

$$q_{ijkl} = c_{ijmn} Q_{mnkl}. \tag{8}$$

Lastly, the electric energy density is expressed as a function of the polarization and electric field and background dielectric constant ( $\epsilon_{ii}^{b}$ ),

$$F_{Electrostatic} = -E_i P_i - \frac{\epsilon_0 \epsilon_{ij}^b}{2} E_i E_j.$$
(9)

where  $\epsilon_0$  is the permittivity of free space.

It should be noted here that limitations of the LGD Phenomenological Theory exist. For example, one such limitation that exists in the presently described theory is the assumption of a single domain existing on the film; while such an approximation works well for some systems and strain states (e.g. compressive strain states) the present approximation does not predict the existence of polydomain phase states. Additionally, some potential may only provide accurate results under small compressive or tensile misfit strains, see e.g. Li *et al* [11].

#### Boundary Conditions:

In the bulk single crystal case, there exist four different types of mechanical boundary conditions that can be applied: stress-free, constrained, applied stress, and applied strain. Application of these boundary conditions depend upon the free energy framework one decides to work in. For example, with Gibbs-free energy the four boundary conditions become,

$$\sigma_{ij} = 0; \tag{10}$$

$$\frac{\partial f_{Bulk}}{\partial \sigma_{ij}} = 0; \tag{11}$$

$$\sigma_{ij} = \sigma_{ij}^{Applied}; \tag{12}$$

$$\frac{\partial f_{Bulk}}{\partial \sigma_{ij}} = -\varepsilon_{ij}^{Applied}.$$
(13)

Alternatively, the boundary conditions in the context of the Helmholtz-free energy become,

$$\frac{\partial f_{Bulk}}{\partial \varepsilon_{ij}} = 0; \tag{14}$$

$$\varepsilon_{ij} = 0;$$
 (15)

$$\frac{\partial f_{Bulk}}{\partial \varepsilon_{ij}} = \sigma_{ij}^{Applied}; \tag{16}$$

$$\varepsilon_{ij} = \varepsilon_{ij}^{Applied}.$$
 (17)

Considering the case of thin films, the boundary conditions become mixed as a ferroelectric epitaxial film has a fixed in-plane strain (both planar and shear) defined by the substrate and the top of the film is described by stress-free conditions. This combination of physical conditions, leads to the following boundary conditions,

$$\varepsilon_{11} = \varepsilon_{11}^m; \varepsilon_{22} = \varepsilon_{22}^m; \varepsilon_{12} = \varepsilon_{21} = \varepsilon_{12}^m,$$
 (18)

$$\sigma_{13} = \sigma_{31} = \sigma_{23} = \sigma_{32} = \sigma_{33} = 0. \tag{19}$$

where  $\varepsilon_{11}^m$ ,  $\varepsilon_{22}^m$ , and  $\varepsilon_{12}^m$  are the so-called misfit epitaxial strains introduced previously. Short circuit boundary conditions are assumed for the electrostatic boundary conditions of the problem.

Utilizing the above boundary conditions that align with the situation one wishes to model, it becomes possible to describe the total free energy density purely in terms of spontaneous polarization. The exact renormalizations of the free energy functions for the cases of (001)-oriented thin films is given in the supplementary information. For other cases, the interested reader is directed to Chen *et al*[6]. The exact renormalization of the free energy function for thin films under arbitrary misfit strains is given in the supplementary information and it matches that asserted by Pertsev *et al.*[20].

### Implementation:

To minimize the energy of the system and determine the equilibrium polar state of the ferroelectric system, we implemented a common evolutionary algorithm known as Differential Evolution (DE henceforth). A variety of authors have provided high-quality reviews into the capabilities of both evolutionary algorithms and in particular, DE. Thus, here we briefly summarize the algorithmic strategy and direct the interested reader to other resources[21–23].

Differential evolution is a member of a class of algorithms known as evolutionary algorithms[21,22]. Other members of this class include the popular Particle Swarm Optimization (PSO), Ant Colony Optimization (ACO), along with the Genetic Algorithm, all of which are discussed in more detail in Refs. [24–27]. DE succeeds by iteratively improving on candidate solutions of a given fitness function, which, in the case of material thermodynamics, is the free energy density of a homogeneous system. It should be noted that DE does not guarantee that an optimal solution is found, however it does sample the multi-dimensional parameter space adequately to allow a solution to be found.

In contrast to other optimization methods, such as the common Newton's method, DE does not require the optimization problem to be differentiable due to its stochastic nature. This characteristic of differential evolution allows for greater applicability than other algorithms such as the Gradient Descent method. However, it should be noted that DE can be sensitive to local minima, thus improvements have been made to the canonical DE algorithm to avoid such clustering and maintain adequate searching of the parameter space and find the global minima[28–31].

The standard DE algorithm consists of four key steps: initialization, mutation, crossover, and selection. Only the final three steps are carried over for the following generation or iteration. The algorithm continues until either the termination criteria is reached, normally this is either a maximum number of iterations or the error is below a specified tolerance. Since the algorithm is searching a *d*-dimensional space, a population of *N d*-dimensional vectors are constructed, and

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each *d*-dimensional vector is a candidate solution. We can describe a specific vector  $x_i^t$  at iteration *t* as,

$$\boldsymbol{x}_{i}^{t} = \left( x_{i,1}^{t}, \dots, x_{i,d}^{t} \right).$$
<sup>(20)</sup>

We must apply bounds to our vector components, and we can initialize our population simply as,

$$x_{i,j} = x_{min,j} + rand[0,1](x_{max,j} - x_{min,j}),$$
(21)

here  $x_{min,j}$  and  $x_{max,j}$  are the minimum and maximum bounds, respectively, of the  $j^{th}$  component of the *d*-dimensional vector  $x_i^t$ , rand[0,1] is a uniformly distributed random number lying between 0 and 1, inclusive.

During the subsequent iterations (also referred to as generations) a *mutant* vector is generated from a selected vector in the population, termed the *target* vector. There are host of mutation strategies, but the two most common are shown below,

rand/1/bin: 
$$v_i^t = x_{r_1}^t + F(x_{r_2}^t + x_{r_3}^t),$$
 (22a)

best/1/bin: 
$$v_i^t = x_{best}^t + F(x_{r_1}^t + x_{r_2}^t).$$
 (22b)

Here  $x_{r_i}^t$  are mutually exclusive random vectors chosen from the population, exclusive of the target vector, and  $x_{best}^t$  is the best candidate solution vector in the population at time *t*, the *F* term is problem dependent but is usually taken in the range [0.4, 0.8] and scales the vector difference of the two randomly chosen vectors. The next step is crossover and is closely related to genetic algorithms where the child vectors have components of the parent vectors. There are two common crossover methods, binomial and exponential. Descriptions of these types are outside the scope of the present report, and thus the interested reader is directed to the references[22]. The new so-called *trial* vector is expressed as,

$$\boldsymbol{u}_{i,j}^{t} = \begin{cases} \boldsymbol{v}_{i,j}^{t} \text{ if } j = K \text{ or } rand[0,1] \leq Cr, \\ \boldsymbol{x}_{i,j}^{t} \text{ otherwise.} \end{cases}$$
(23)

Here *K* is a randomly chosen integer in the range [1, d], *Cr* is the crossover parameter and normally takes a value in the range [0.5, 0.8]. This approach ensures at least one component of the new *trial* vector is from the *mutant* vector created in **Eq. (22a)** or **Eq. (22b)**. The fitness of the *trial* vector is then compared to the *target* vector using a simple elitist selection criterion,

$$x_i^{t+1} = \begin{cases} u^t & \text{if } f(u^t) \le f(x_i^t), \\ x_i^t & \text{otherwise.} \end{cases}$$
(24)

where f(.) is merely the objective function to be minimized or maximized. While the standard DE algorithm works well for most problems, we have implemented a few changes to the code to assist in converging to a solution more quickly. We have implemented a so-called *Information-Preservation* scheme which replaces the simple elitist selection criteria in **Eq. (24)**[28,30]. All the objective function evaluations in each generation along with all of the *trial* vectors are stored, creating a population of size 2N. Only the N best vectors are kept from this larger population. It has been demonstrated that such an information scheme can improve the convergence of DE on unimodal landscapes, which can be achieved in symmetry restricted systems such as ferroelectrics[30].

The other adjustment we have included is a scaled gradient descent perturbation vector (p) to the *trial* vector in the form of [32],

$$H_f(\boldsymbol{u}_i^t)\boldsymbol{p} = -\nabla_f(\boldsymbol{u}_i^t). \tag{25}$$

Here  $H_f$  is the hessian of the objective function and  $\nabla_f$  is the gradient of the objective function and  $u_i^t$  is a given *trial* vector. Other studies have demonstrated that this is an effective method for increasing the convergence speed of DE[32,33]. A more complete study of this DE variant with both benchmark functions and materials specific calculations will be described elsewhere.

## **Case Studies**

A variety of validation studies have been performed to test the accuracy and capabilities of the Q - POP - Thermo software. To accomplish this, we consider the following case studies: effect of applied stress on phase transitions of bulk BaTiO<sub>3</sub>, electromechanical properties of BaTiO<sub>3</sub> thin films, polarization of (111)-textured BaTiO<sub>3</sub>, the electrocaloric strength of lead-free ferroelectrics and the common temperature-misfit strain domain phase diagram.

# Effect of Applied Stress on Phase Transitions of Bulk BaTiO<sub>3</sub>

It is widely known that the phase transition of ferroelectric materials can be modified by the influence of external fields whether that is elastic, electric, or thermal fields. For example, Wang *et al.* have examined the influence of hydrostatic stress on the ferroelectric properties of BaTiO<sub>3</sub> single crystals using LGD theory based on earlier experimental measurements[10]. It was shown that increasing the hydrostatic stress on the crystal not only decreases the Curie temperature, the temperature for ferroelectric-paraelectric transition, but also influences the temperature of the inter-ferroelectric phase transitions. This effect is not limited to BaTiO<sub>3</sub> as other materials such as PbTiO<sub>3</sub> and PZT show similar effects[34–37]. Thus, the effect of hydrostatic pressure on the domain structure of single crystal materials is an excellent test case for our program.

Utilizing the BaTiO<sub>3</sub> thermodynamic potential presented by Wang *et al.*, we have calculated the magnitude of the spontaneous polarization of bulk single crystals, **Figure 1**[10]. It is obvious that as the hydrostatic pressure is increased, both the magnitude of the polarization and the phase transition temperatures continuously decrease as well. This is consistent with the work of Wang demonstrating the capabilities of Q-POP-Thermo when applying a pressure to the ferroelectric single crystals.



*Figure 1* – a) Spontaneous polarization of BaTiO<sub>3</sub> under applied hydrostatic stress. The open circles are data points from [10]; b) Phase diagram of BaTiO<sub>3</sub> as a function of hydrostatic pressure and temperature. Experimental data points are taken from [38].

Additionally, we have also compared both the piezoelectric and dielectric susceptibility tensors for further validation of the bulk thermodynamic model. It was seen that these results match closely with previous works [11,39]. As seen in Figure 1, it is apparent that as the hydrostatic pressure increases, the number of phase transitions reduces as well. For example, when the applied hydrostatic pressure is above ~5 GPa but below ~6 GPa a rhombohedral state cannot form and only the orthorhombic and tetragonal ferroelectric states are accessible. Similarly, at higher pressure, above ~6 GPa, the BaTiO<sub>3</sub> system will only form a tetragonal ferroelectric state. Using the proposed software we determine the phase transitions with respect to both pressure and temperature and compare those as well. It was seen in both Q-POP-Thermo and Wang et al. that the critical pressure where the rhombohedral phase disappears is located at ~5.1 GPa, whereas the orthorhombic phase lasts until nearly 5.8 GPa, and the tetragonal phase transitions to the cubic phase at ~6.4 GPa. Turning next toward the phase transition temperatures, we see that at zero hydrostatic pressure, the rhombohedral to orthorhombic phase transition takes place at 207K for both the proposed software and the preexisting experimental work. The phase transition temperature for the orthorhombic to tetragonal and tetragonal to paraelectric phases are 280K and 396K, respectively, and are realized using the proposed software. Indicating that the software accurately predicts both the phase transition temperatures and pressures.

#### Piezoelectric Coefficients of BaTiO<sub>3</sub> Thin Films

The piezoelectric coefficients of perovskite ferroelectric are generally much larger than non-ferroic piezoelectrics and are also highly anisotropic, allowing for high-performance sensing, actuating, and energy harvesting applications [40,41]. The piezoelectric coefficient depends on the polar state of a ferroelectric crystal; the rotation and elongation of the spontaneous polarization can considerably influence the piezoelectric properties. A great deal of work has been devoted to study the piezoelectric tensor of BaTiO<sub>3</sub> system, therefore providing a great case study for the proposed software[2,42,43]. It should be noted here that the application of an applied stress or strain changes the symmetry of the system, for example applying a biaxial stress to a rhombohedral system would yield a monoclinic type symmetry. We note here that the properties calculated by Q-POP-Thermo are calculated in the cubic reference frame. Thus, the interested reader could quickly transform the piezoelectric (or dielectric) tensor into the reference frame of another symmetry (i.e. orthorhombic or rhombohedral) to compare with previous works, such as Budimir *et al*[44].

Following the work of previous authors, such as Emelyanov *et al.* and Wu *et al.*, one can determine the piezoelectric coefficients from the thermodynamic free energy of the system, i.e [42,45].

$$d_{in} = \frac{\partial \varepsilon_n}{\partial E_i} = \sum_{j=1}^3 \frac{\partial \varepsilon_n}{\partial P_j} \eta_{ij}, \tag{26}$$

here the strains are defined in Voigt notation and can be defined using the Gibbs free energy, either **Eq. (1)** for bulk or **Eq. (2)** for thin films, relation between stress and strain (i.e.,  $\frac{\partial G}{\partial \sigma_i} = -\varepsilon_i$ ) and  $\eta_{ij}$  is the dielectric susceptibility tensors defined by,

$$\eta_{ij} = \left[\frac{\partial^2 G}{\partial P_i \partial P_j}\right]^{-1}.$$
(27)

Using the above relations along with the free energy defined previously, the piezoelectric coefficients of any material can be determined rather quickly. It should be noted here that if one chooses to define the free energy in the Helmholtz framework, similar equations can be derived for the other piezoelectric tensor coefficients. Q-POP-Thermo uses the Gibbs energy framework for all the necessary calculations.

The piezoelectric coefficients for BaTiO<sub>3</sub> were calculated as a function of misfit strain at 298 K. We note here that the piezoelectric coefficients calculated herein, do not account for the symmetry of the applied epitaxial strain and instead are calculated using the Maxwell relations above with respect to the polarization and other material properties. It is obvious that there exist multiple stable phases, as depicted in **Figure 2**. A tetragonal phase ( $T_c = (0,0,P_3)$ ) is stable at compressive misfit strain, whereas at misfit strains near zero a monoclinic phase ( $M(r) = (P_1, P_2, P_3)$ , where  $P_1 = P_2 \neq P_3$ ) forms. In the tensile regions of the phase diagram the elastic constraints cause an in-plane orthorhombic structure to form ( $O_{AB} = (P_1, P_2, 0)$ , where  $P_1 = P_2$ ). It can be seen that a large increase in the piezoelectric coefficients occur at phase transitions, which is intrinsic to ferroelectric systems. Additionally, similar trends were seen between our calculations here and the current literature, where near 0.0% misfit strain there is a drastic increase in the d<sub>33</sub> piezoelectric coefficient before becoming 0.0 at tensile strains.[42,43]. The actual transition strains and temperatures are different due to slightly different thermodynamic potentials, elastic constants, and film growth conditions which can all play a role in the calculation of the piezoelectric properties of a material[42,43].



Figure 2 – (Color Online) Piezoelectric coefficients of (001)-oriented single-domain BaTiO3 thin films.

Understanding the location of these phase boundaries in thin film systems can allow researchers the ability to control where such phase transitions occur. Therefore, allowing unprecedented control in manipulating the properties of a given material, ultimately leading to next generation nano-devices and applications.

# Polarization of (111)-Oriented BaTiO<sub>3</sub> Thin Films

To test the crystal rotation functionality of Q-POP-Thermo, we have calculated the polarization components of (111)-textured BaTiO<sub>3</sub> thin films. Quite a few studies have been devoted to unlocking the potential of rotated crystal systems particularly with respect to electrocaloric properties[42,46–48]. Xu *et al.* demonstrated that there a larger region of dielectric response occurs in (111)-oriented PZT thin films[49].

As a case study, we calculated the temperature dependence of polarization of (111)-oriented BaTiO<sub>3</sub> thin films. The results agree well with the work of Wu *et al.* who studied the effect of crystal orientation of the same system, providing validity to the proposed software[42]. It is seen in **Figure 3** that upon reorienting the crystal, only two phases become present: a rhombohedral phase (R,  $P_1 = P_2 = P_3 \neq 0$ ;  $P'_1 = P'_2 = 0$ ,  $P'_3 \neq 0$ ) and a monoclinic phase (M(r),  $P_1 = P_2 > P_3 \neq 0$ ;  $P'_2 \neq P'_3 > P'_1 = 0$ ) compared to the (001)-textured film that demonstrates three phases (see previous case

study). It is also seen that the phase transition strain is independent of temperature. Such temperature independent phase boundaries hint toward improved thermal stability of functional properties such as dielectric, piezoelectric, and ferroelectric properties. Additionally, these results agree with that of Angsten and coworkers as well who performed first-principles calculations of oriented ferroelectric films[50].



Figure 3 – (Color Online) Polarization of (111)-Oriented single-domain BTO Epitaxial Thin Films. Electrocaloric Performance of Doped-BaTiO<sub>3</sub> Systems

Recently, the possibility of solid-state refrigeration technologies has been of great interest. One such method of solid-state refrigeration is through the electrocaloric effect (ECE). The electrocaloric effect refers to the adiabatic temperature change of a material when subjected to an electric field. An example is the discovery of colossal ECE in PZT films by Mischenko *et al.*[51]. Since then, many different ferroelectric perovskites, such as BaTiO<sub>3</sub>, Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> (NBT), and KNaNbO<sub>3</sub> (KNN), have been studied for potential ECE uses[52–56].

As an additional case study for Q-POP-Thermo, the electrocaloric performance of BaTiO<sub>3</sub>-based solid solutions is evaluated. Huang *et al.* demonstrated the use of strontium doping on the A site  $((Ba_{1-x},Sr_x)TiO_3, BSTO)$  as a potential ECE enhancement mechanism, while Luo and coworkers presented similar data for the Barium Titanate Stannate system  $(Ba(Ti_{1-x}, Sn_x)O_3, BTSO)[15,57]$ . Here, we present results for three different BaTiO<sub>3</sub>-based solid solutions:  $(Ca_x, Ba_{1-x})TiO_3$  (BCTO), BSTO and Ba $(Ti_{1-x}, Zr_x)O_3$  (BZTO) for the case of bulk single crystal systems.

Using Maxwell Relations, it is straightforward to calculate the entropy change from a potential energy function, i.e.

$$\Delta S = -\frac{1}{\rho} \frac{\partial F(\mathbf{P}, T, \sigma_{ij}, E_i)}{\partial T},$$
(28)

here  $\rho$  is the mass density and is listed in **Table 1** for each of the solutions above. The electrocaloric effect can then be defined by,

$$\Delta T_{Elec} = \frac{T}{c_p} \left( \Delta S(\boldsymbol{P}, T, \sigma_{ij}, E_i = E^{app}) - \Delta S(\boldsymbol{P}, T, \sigma_{ij}, E_i = 0) \right),$$
(29)

where  $c_p$  is the heat capacity at constant pressure of the material, and  $E^{app}$  is the applied electric field. Using these relations, it is then possible to determine the temperature change a system will undergo due to the electrocaloric effect. Similarly, one could also study the elasto-, flexo-, and combined caloric effects to find methods to enhance the cooling properties of ferroelectrics.

Table 1 - Material properties utilized for electrocaloric studies.

Property/Material	(Ba <sub>1-x</sub> , Ca <sub>x</sub> )TiO <sub>3</sub>	(Ba₁₋x, Sr <sub>x</sub> )TiO₃	Ba(Ti <sub>1-x</sub> , Zr <sub>x</sub> )O <sub>3</sub>
$ ho \left(\frac{g}{cm^3}\right)$	5.89(1-x) + 3.83x	5.89(1-x) + 4.96x	5.89(1-x) + 5.95x
$c_p\left(\frac{J}{kg\cdot K}\right)$		500	
Thermodynamic Potential	[14]	[15]	[13]

Four different electric field magnitudes were applied to the single crystal models:  $2.5 \frac{MV}{m}$ ,  $5.0 \frac{MV}{m}$ ,  $7.5 \frac{MV}{m}$ , and  $10 \frac{MV}{m}$ . Zero-stress boundary conditions were utilized as well for all calculations.

The Q - POP - Thermo software can output the entropy based on **Eq. (25)**. From there one can apply **Eq. (26)** to calculate the adiabatic temperature change. Similarly, since Q-POP-Thermo can output the total polarization, it is also possible to calculate the ECE via

$$\Delta T = -\frac{T}{\rho} \int_{0}^{E_{app}} \frac{1}{c_E} \left(\frac{\partial P}{\partial T}\right)_E dE.$$
(30)

Here  $\left(\frac{\partial P}{\partial T}\right)_{E}$  can be fitted to either 4<sup>th</sup> or 6<sup>th</sup> order polynomials to allow for accurate determination of the temperature change, and  $c_{E}$  is the heat capacity at constant applied electric field.



Figure 4 - Electrocaloric response of Ba(Ti, Zr)O<sub>3</sub>(A-B), (Ba, Sr)TiO<sub>3</sub> (C-D), (Ba, Ca)TiO<sub>3</sub> (E-F) single crystals.

The results of the electrocaloric calculations can be seen in **Figure 4**. It is noticeable with the addition of both Zr and Sr that the electrocaloric effect is suppressed, which agrees with previous studies. However, the opposite is true for doping BaTiO<sub>3</sub> with *Ca* atoms on the A site cation, which leads to a slight improvement in the electrocaloric performance.

It is noticeable that the peak broadens with increasing Sr mol factions along with an increase in the electric field magnitude, a similar trend was demonstrated in [15], **Figure 4C-D**. This broadening of the ECE peak could prove useful in a variety of room temperature cooling techniques, dues to this wide shape and the high reversible temperature change of ~2 K. It should be noted that the results here agree qualitatively with those seen in studies such as Dai *et al.*; however, it has been demonstrated that domain walls can decrease the ECE, which explains the difference in  $\Delta T_{EC}$  presented here and elsewhere in the literature[15,58,59].

For the case of BZT, **Figure 4A-B**, it is noticeable that single crystal undergoes several different phase transitions depicted by multiple sharp peaks in the ECE plots. Such phase transitions allow for a wide range of potential uses in ECE technologies. For example,  $Ba(Ti_{0.95}, Zr_{0.05})O_3$  demonstrates a large peak of ~2 K (at 5.0 MV/m) at ~ 390 K (the Curie Temperature of this particular solution), but also possesses a smaller peak of ~1 K at 300 K (again at 5.0 MV/m). In addition, the location of these secondary peaks changes with respect to the applied electric field, allowing for unprecedented access to manipulating the material system to attain adequate performance, e.g. the phase transition (of  $Ba(Ti_{0.95}, Zr_{0.05})O_3$ ) with an applied field of 2.5 MV/m happens ~315 K, but at the highest field tested (10.0 MV/m) the phase transition happens near room temperature (~298 K), while also broadening the peak of ECE. Between careful preparation of the BTO – BZO solution and proper application of an electric field, the ECE properties of BZT ferroelectrics can be tuned for optimal performance.

Lastly, the ECE for the BCTO system is presented in **Figure 4E-F**. As predicted by previous authors there is little to no shift in the Curie Temperature of the low concentrations of Ca studied here. However, it is evident that the higher concentrations of Ca can lead to higher ECE performance. This performance can be exploited to tailor the material to achieve the necessary performance at or near the Curie temperature. While not studied here, it has been demonstrated that hydrostatic pressure decreases the Curie temperatures of materials. Seeing the large

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temperature changes demonstrated here (> 3 K), it could prove advantageous to study the effect of hydrostatic pressure on the BCTO system regarding caloric performance. As stabilizing a high ECE BCT system could be boon for many different solid state cooling technologies.

# Temperature – Misfit Strain Phase Diagrams of Ba(Zr, Ti)O<sub>3</sub> Thin Films.

Due to the potential applications in next generation devices, thin ferroelectric films are continually studied from computational and experimental angles[40,60]. Understanding the effect of epitaxial strain on the phase transitions and phase stability of ferroelectric materials is paramount to controlling the behavior of such materials. Thus, a method for accurately calculating such phase diagrams is necessary. Therefore, as a final case study for the use of Q-POP-Thermo, we have calculated the phase diagrams of the BZT system with regard to both temperature and biaxial epitaxial strain for two compositions.



Figure 5 – (Color Online) Monodomain Temperature - Misfit Strain Phase Diagram of A) Ba(Tio.95, Zro.05)O3 and B) Ba(Tio.90, Zro.10)O3 thin films using the potential recently reported by Huang et al. [13].
Using a recently reported potential, the temperature misfit strain phase diagrams are demonstrated in Figure 5[13]. It is evident that increasing the concentration of Zr in the system decreases the ferroelectric-paraelectric transition temperature, as well as changes the aspect

ratio of the rhombohedral phase region. Such changes in the phase diagram could prove useful toward growing such films for specific applications or optimally adjusting phase transition temperatures. A more-through polydomain study of these systems is underway and be reported elsewhere

### **Conclusions and Future Work**

We have introduced and described Q-POP-Thermo, an open-source Python program for solving the thermodynamics of ferroelectric single crystals and thin films, as well as calculate the accompanying properties. Differential evolution as a solving method for these types of problems is introduced and shown to be effective. A variety of case studies are demonstrated as well to test the validity of the program and the results are comparable to previous materials studies.

Phase diagram calculations incorporating multiple domains is under development to better compare with the phase field method and provide a faster *a priori* method for approximating domain phase diagrams and other ferroelectric properties, e.g., by incorporating the strain phase separation described by Xue *et al.* and incorporating the boundary conditions proposed by Roytburd and coworkers[61–64].

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# Contributions

The bulk of the code was written by J.A.Z. with inspiration from a previous work by B.W. All calculations presented, along with the development of the advanced DE algorithm were completed and implemented by J.A.Z. B.W. suggested and helped define validation case studies for the work. L.Q.C. supervised the research and suggested regions of improvement. J.A.Z. drafted the manuscript and all authors were involved in the editing, discussion of results, and submission of the manuscript.

## **Conflicts of Interest**

The authors state no known conflicts of interest regarding the work presented here.

# Data and Code Availability

The software introduced herein is available for download along with documentation and the examples presented here at https://gitlab.com/jzorn164/qpopthermo.

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# Supplementary Information

# 1. Renormalized Thin Film Constants

The renormalized Landau constants after the application applicable boundary conditions for a thin film structure are outlined below:

$$\tilde{G} = \alpha_1^* P_1^2 + \alpha_2^* P_2^2 + \alpha_3^* P_3^2 + \alpha_6^* P_1 P_2 + \alpha_{11}^* (P_1^4 + P_2^4) + \alpha_{33}^* P_3^4 + \alpha_{13}^* (P_1^2 P_3^2 + P_2^2 P_3^2) + \alpha_{12}^* P_1^2 P_2^2 + \alpha_{111}^* (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} \left( P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2) \right) + \alpha_{123} P_1^2 P_2^2 P_3^2 + \alpha_{111}^* (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} \left( P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2) \right) + \alpha_{123} P_1^2 P_2^2 P_3^2 + \alpha_{111}^* (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} \left( P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2) \right) + \alpha_{123} P_1^2 P_2^2 P_3^2 + \alpha_{111}^* (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} \left( P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2) \right) + \alpha_{123} P_1^2 P_2^2 P_3^2 + \alpha_{112}^* (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} \left( P_1^6 (P_2^6 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2) \right) + \alpha_{123} P_1^2 P_2^2 P_3^2 + \alpha_{112}^* (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} \left( P_1^6 (P_2^6 + P_3^6) + P_2^6 (P_1^6 + P_3^6) + P_3^6 (P_1^6 + P_3^6) + \alpha_{123} P_1^2 P_2^2 P_3^2 + \alpha_{123} P_1^2 P_3^2 + \alpha_{123} P_1^2 P_3^2 + \alpha_{123} P_1^2 P_3^2 + \alpha_{123} P_1^2 P_2^2 P_3^2 + \alpha_{123} P_1^2 P_3^2 + \alpha_{123} P_3^2 + \alpha_{123} P_1^2 P_3^2 + \alpha_{123} P_3^2 + \alpha_$$

$$G_8(P_1, P_2, P_3) + \frac{(s_{11}(u_{11}^2 + u_{22}^2) - 2s_{12}u_{11}u_{22})}{2(s_{11}^2 - s_{12}^2)} + \frac{u_{12}^2}{2s_{44}};$$
 (SI. 1)

Where,

$$\alpha_1^* = \alpha_1 + \frac{\left(u_{11}(Q_{12}s_{12} - Q_{11}s_{11}) + u_{22}(Q_{11}s_{12} - Q_{12}s_{11})\right)}{s_{11}^2 - s_{12}^2},$$
(SI. 2)

$$\alpha_2^* = \alpha_1 + \frac{\left(u_{22}(Q_{12}s_{12} - Q_{11}s_{11}) + u_{11}(Q_{11}s_{12} - Q_{12}s_{11})\right)}{s_{11}^2 - s_{12}^2},$$
(SI. 3)

$$\alpha_3^* = \alpha_1 - \frac{(Q_{12}(u_{11}+u_{22}))}{s_{11}+s_{12}},$$
(SI. 4)

$$\alpha_6^* = -\frac{Q_{44}}{s_{44}} u_{12},\tag{SI. 5}$$

$$\alpha_{11}^* = \alpha_{11} + \frac{1}{2} \frac{1}{s_{11}^2 - s_{12}^2} \left( (Q_{11}^2 + Q_{12}^2) s_{11} - 2Q_{11}Q_{12}s_{12} \right),$$
(SI. 6)

$$\alpha_{12}^* = \alpha_{12} + \frac{1}{s_{11}^2 - s_{12}^2} \left( (Q_{11}^2 + Q_{12}^2) s_{12} - 2Q_{11}Q_{12}s_{11} \right) + \frac{Q_{44}^2}{2s_{44}}, \tag{SI. 7}$$

$$\alpha_{13}^* = \alpha_{12} + \frac{Q_{12}(Q_{11} + Q_{12})}{s_{11} + s_{12}},$$
(SI. 8)

$$\alpha_{33}^* = \alpha_{11} + \frac{Q_{12}^2}{s_{11} + s_{12}}.$$
(SI. 9)

It is apparent that upon application of isotropic misfit strain with zero misfit shear strain that the results match that of Pertsev *et al.*[20].

# 2. Derivation of Electrostrictive Coefficients for both Helmholtz and Gibbs Free Energy Frameworks

We begin with the free energy for the unpolarized and unstrained crystal as a reference, we can write this free energy as a function of strain and polarization, i.e.

$$\begin{split} F(P,\varepsilon) &= \frac{1}{2} \alpha_{ij} P_i P_j + \frac{1}{3} \beta_{ijk} P_i P_j P_k + \frac{1}{4} \gamma_{ijkl} P_i P_j P_k P_l + \frac{1}{5} \delta_{ijklm} P_i P_j P_k P_l P_m + \cdots \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \\ &- \frac{1}{2} q_{ijkl} \varepsilon_{ij} P_k P_l. \end{split}$$

Here  $\alpha_{ij}$ ,  $\beta_{ijk}$ ,  $\gamma_{ijkl}$ , and  $\delta_{ijklm}$  are the phenomenological Landau expansion coefficients, and  $c_{ijkl}$ , and  $q_{ijkl}$  are the elastic and electrostrictive constant tensors respectively. All coefficients are assumed to be constant with the exception of  $\alpha_{ij}$  which is linearly proportional to temperature. If the parent phase is centrosymmetric, as the case with perovskite ferroelectrics, all of the odd terms fall out resulting in,

$$F(P,\varepsilon) = \frac{1}{2}\alpha_{ij}P_iP_j + \frac{1}{4}\gamma_{ijkl}P_iP_jP_kP_l + \dots + \frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} - \frac{1}{2}q_{ijkl}\varepsilon_{ij}P_kP_l.$$

The spontaneous polarization can be solved by setting the strain to zero and solving,

$$\frac{\partial F(P,\varepsilon=0)}{\partial P}=0.$$

The stress can be defined by,

$$\left(\frac{\partial F}{\partial \varepsilon_{ij}}\right)_{T,P_k} = \sigma_{ij},$$

Or

$$\sigma_{ij} = c_{ijkl} \varepsilon_{kl} - \frac{1}{2} q_{ijkl} P_k P_l.$$

Setting the stress to zero, one can solve for the spontaneous strain,

$$\varepsilon_{ij}^0(P_k) = \frac{1}{2} \frac{q_{ijkl} P_k P_l}{c_{ijkl}}.$$

Experimentally, this spontaneous strain is given by,

$$\varepsilon_{ij}^0(P_k) = Q_{ijkl}P_kP_l.$$

Thus it is obvious that

$$q_{ijkl} = 2c_{ijkl}Q_{ijkl}.$$

3. Transformation Matrix

The ZYZ Transformation Matrix can be defined by,

$$\begin{bmatrix} \cos(\phi)\cos(\psi)\cos(\theta) - \sin(\phi)\sin(\psi) & -\sin(\phi)\cos(\psi)\cos(\theta) - \sin(\psi)\cos(\phi) & \sin(\theta)\cos(\psi) \\ \sin(\phi)\cos(\psi) + \sin(\psi)\cos(\phi)\cos(\theta) & \cos(\phi)\cos(\psi) - \sin(\psi)\sin(\phi)\cos(\theta) & \sin(\psi)\sin(\theta) \\ & -\sin(\theta)\cos(\phi) & \sin(\phi)\sin(\theta) & \cos(\theta) \end{bmatrix}$$