Project Report: PH301

A Comprehensive Study on Ferroelectric Phase Transitions in $BaTiO_3$ Through Landau Theory

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Abstract

Perovskites such as $BaTiO_3$ are an important class of materials extensively studied for their amazing ferroelectric and piezoelectric properties and have found their use in several devices such as sensors and memory devices such as DRAMs. In this direction, we present a project report on the theoretical and experimental study of $BaTiO_3$. We report an experimentally observed Curie-Temperature, $T_C \sim 120^oC$ from the temperature-dependent dielectric permittivity data (ϵ_R). The 13 mm $BaTiO_3$ was synthesized through the standard solid-state reaction route using the binary-oxide precursors Barium Oxide (BaO) and Titanium Oxide (TiO_2) powders. It's dielectric measurements were taken with a parallel-plate capacitor geometry set-up. For the theoretical comparison, we employed the Landau-Devonshire(LD) thermodynamical theory of ferroelectrics. The LD potential was expanded up to the 6^{th} order in the Taylor Series expansion. Following which, the 1-Dimensional case was analyzed analytically and yielded T_C=109.61^{o}C. The 3-D case was solved numerically using a python script utilizing the Newton-Jacobi method of solving a system of higher-order polynomials, this led to T_C=118^{o}C. All the three values were compared, signifying the success of the LD theory in explaining the phase transitions of the ferroelectric $BaTiO_3$.

Contents

1 Acknowledgement

This academic project was supported by the Indian Institute of Technology Guwahati. We thank our Professor M.C.Kumar Sir who provided insight and expertise that greatly assisted the study and motivated us to learn about ferroelectric phase transitions from a statistical point of view. We thank our group members for their assistance with the various section of the project report and the teamwork they showcased. We would also like to show our gratitude to Professor Subhash Thota for allowing us to utilize his lab's resources to synthesize our sample and collect our experimental data.

2 Motivation

The major motivation behind this project was to understand the process of phase transition as it cannot be explained with any conventional theories, we need a statistical mechanics approach to deal with this problem. The search for an answer to our questions led us to Landau theory of phase transition, an idea so simple yet so profound that even a basic analysis of Landau potential reveals so many critical phenomenons.Also the fact that discontinuities exist in nature of which phase transition is an example has a very metaphysical implication.
We wanted to do some experimental analysis and numerical analysis too. Hence we found a perfect opportunity to analyse a phase transition occuring in ferroelectrics where it transforms into a paraelectric at critical temperature. This topic is not covered in conventional classes, as everyone mostly focuses on its well established counterpart ferromagnetism. While doing literature review, we came to know about its applications in emerging technologies which added to our thrust.

3 Introduction

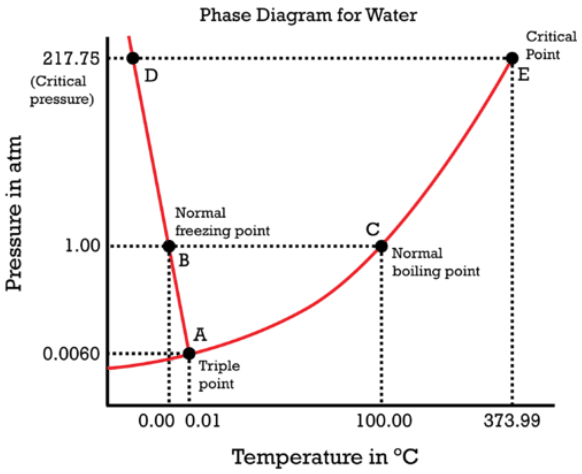
The aim of this project is to systematically study the Landau Theory of Phase Transitions and explore its applications in the domain of condensed matter physics by using this theory to probe the nature of phase transitions in ferroelectric systems. Through the sections of the introduction, we introduce the reader by delving into the depths of phase transitions, Landau Theory and Ferroelectricity before beginning our study on the relation between these concepts.

3.1 Phase Transitions

When dealing with most systems, changing it's macroscopic parameters may result in an abrupt or discontinuous change in the physical properties of the system. For example, a

system under the influence of a refrigerator may abruptly change from a liquid to a solid or a heater may change a ferromagnetic system to a paramagnetic one. These abrupt changes are called Phase Transitions.

These transitions occur when the thermodynamic free energy function of a system is



The region between ACE and the temperature axis, signifies the gaseous phase, the region between ABD and the pressure-axis is the ice phase, while the remaining region is water in it's liquid phase.

Figure 1: The phase diagram for water in the Pressure, Temperature phase space

non-analytic for a certain set of thermodynamic parameters. At the phase transition point (Also called the critical point) of n-number of phases, all the phases in question possess an identical free energy and hence we say that at the critical point, the phases are said to co-exist as all of them are equally likely to occur. For example, in the case of water, beyond the critical temperature, there is *no* pressure that is high enough to liqueify the gas.

At the critical point, the characteristic of the curve in the phase diagram is given as:

$$(\frac{\partial P}{\partial V})_T = 0$$

$$(\frac{\partial^2 P}{\partial V^2})_T = 0$$

Solving these equations for the state-equation of the system, we obtain the critical point. For a gas, we solve this for the *van der Waals* equation and obtain the following critical points:

$$T_C = \frac{8a}{27Rb}, V_C = 3nb, P_C = \frac{a}{27b^2}$$

Similarly, we can obtain the critical point of any system from its phase diagram and respective equation of state.

Using this definition of phase transitions, the modern classification for phase transitions was developed where classify them into two broad categories:

1. **First-Order Transitions**: These phase transitions can be characterized by their *non-zero* Latent Heat (Λ)-The amount of heat required to transition from one phase to the other given that the macroscopic parameters (e.g Temperature, Pressure) remain constant. The change in the system's parameters (Entropy, volume, etc) are

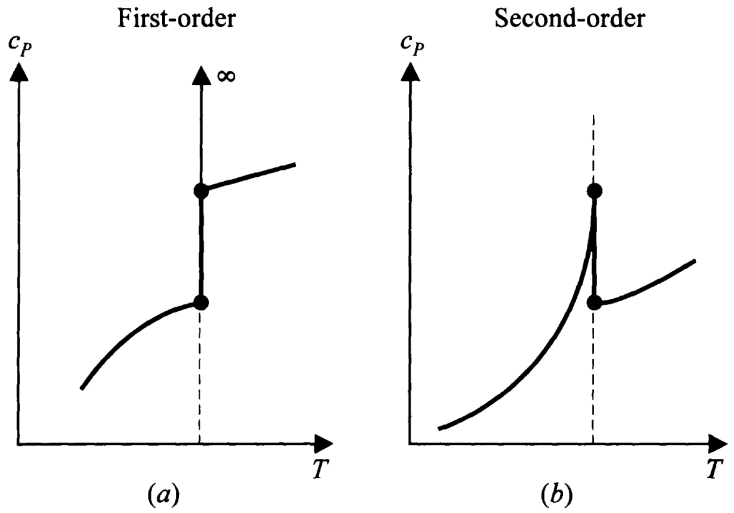


Figure 2: The c_P vs T variation for a. A first-order transition and b.A second-order transition

discontinuous. Basically, the *order-parameter* (s) which can be written as $\partial G/\partial T$ is discontinuous across the transition, where G is Gibb's Free Energy. Familiar examples include the melting of ice or the boiling of water.

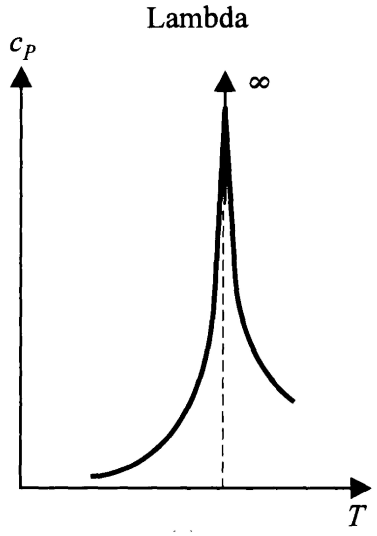
2. **Second-Order Transitions**: These transitions are "continuous" in a sense that the order-parameter as previously defined is continuous across the transition, however, it's derivative $\partial^2 G/\partial T^2$ is not. Some examples include the ferromagnetic transition and superconducting transition.

For higher-order phase transitions, the system's quantities like c_P and β undergo *finite* changes since:

$$\frac{c_P}{T} = (\frac{\partial s}{\partial T})_P = -(\frac{\partial^2 G}{\partial T^2})_P$$

$$\beta\nu = (\frac{\partial v}{\partial T}) = (\frac{\partial^2 G}{\partial T \partial P})_{T,P}$$

The variation of c_P with T for first and second order phase transitions is presented in Fig 1a and 1b respectively.
This brings us to another kind of phase transition called the *lambda* transition, which is a continuous phase transition characterized by continuous T, P and G and an infinite value for the c_P and β parameters.The parameter c_P shows an asymptotic behaviour at the critical temperature as shown in Fig 2. It's important to note here that c_P here is the heat capacity of the system and β is the thermodynamic beta factor which can be written as $\frac{1}{k_B T}$ or $\frac{1}{k_B}(\frac{\partial S}{\partial E})_{V,N}$.



An interesting feature to note about lambda transitions is that the c_P starts to rise sharply before the critical point is reached, almost as if it "anticipates" the incoming transition. This is indicative of high-correlative behaviour within the system. Lambda transitions can be used to explain the ferroelectricity in certain crystals such as Rochelle Salts [2].

Figure 3: The c_P vs T variation for a lambda transition

3.2 Ferroelectricity

Ferroelectricity, analogous to ferromagnetism, is the property of a material to have spontaneous electric polarization which can be reversed on application of an external electric field. This is much like how in ferromagnets, the ferromagnetic material possesses spontaneous magnetization that is reversed upon applying an external magnetic field. It was discovered in 1920 in Rochelle Salts by American physicist Joseph Valasek [1].
Most materials, on being electrical polarized, induce a linear polarization P that is directly proportional to the applied electric field E as shown in Fig 2. Some materials, referred to as paraelectric materials, have heightened nonlinear polarisation. The slope of the polarisation curve, which corresponds to the electric permittivity, is a function of the external electric field rather than being constant, as it is with linear dielectrics as shown in Fig 3.

Ferroelectric materials exhibit a spontaneous nonzero polarisation even when the applied field E is zero, in addition to being nonlinear. Ferroelectrics are distinguished by the ability of the spontaneous polarisation to be reversed by an appropriately strong applied electric field in the opposite direction. As a result, the polarisation is reliant on both the current electric field and its history, producing a hysteresis loop. By comparison to ferromagnetic materials, which have spontaneous magnetization and show comparable hysteresis loops, they are known as ferroelectrics.
The Curie temperature (T_C), above which spontaneous polarisation disappears and the ferroelectric crystal changes into the paraelectric state, is the typical phase transition temperature below which materials typically exhibit ferroelectricity.
We will now try to explore a theoretical model to describe ferroelectricity based on the Ginzburg-Landau Theory. The Free-Energy of the ferroelectric material (G) in the ab-

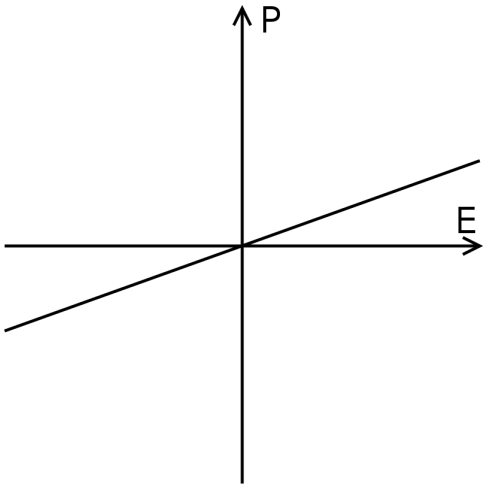


Figure 4: The P vs E variation for a linear dielectric

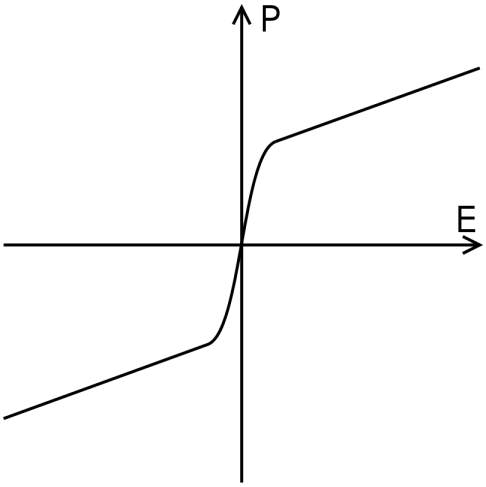


Figure 5: The P vs E variation for a paraelectric material

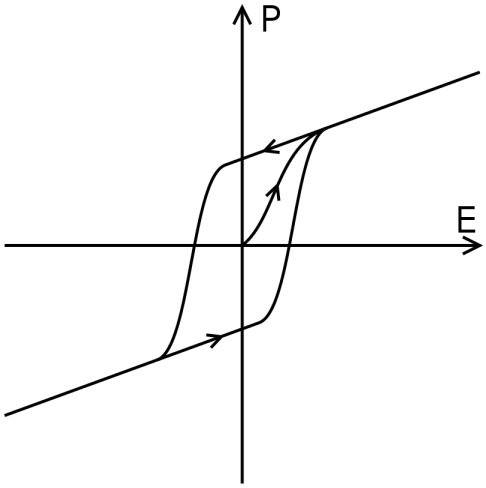


Figure 6: The P vs E variation for a linear dielectric

These materials find their various applications in tunable capacitors. Another interesting application of such materials due to their spontaneous polarization is in ferroelectric RAM chips as the hysterisis effect that is observed in the polarization loop can be used as a memory function.

sence of an applied electric field E and stress, the functional, also called the Landau-Devonshire potential, can be written in the sixth-order expansion as:

$$\begin{aligned}\Delta G = \frac{1}{2}\alpha_0(T-T_0)(P_x^2+P_y^2+P_z^2) + \frac{1}{4}\alpha_{11}(P_x^4+P_y^4+P_z^4) \\ + \frac{1}{2}\alpha_{12}(P_x^2P_y^2+P_y^2P_z^2+P_z^2P_x^2) + \frac{1}{6}\alpha_{111}(P_x^6+P_y^6+P_z^6) \\ + \frac{1}{2}\alpha_{112}[P_x^4(P_z^2+P_y^2)+P_y^4(P_x^2+P_z^2)+P_z^4(P_x^2+P_y^2)] + \frac{1}{2}\alpha_{123}P_x^2P_y^2P_z^2\end{aligned}$$

Where P_x,P_y and P_z are the polarization in their respective directions and the coefficients α_i,α_{ij} and α_{ijk} are consistent with the crystal symmetry of the lattice structure. These equations are used to investigate the domain formations and ferroelectric phase transitions and will be discussed in further detail in the coming sections.

3.3 Landau Theory

One of the first model applied to explain macroscopic parameters of ferroelectricity was Landau theory. We know that the bulk phase of any crystal can defined in terms of its macroscopic parameters such electric field (E), polarization (P), temperature (T), strain (η) and stress (σ). Some of these parameters are inter-related for e.g P and E. One thing to note is that Landau theory can only be applied to understand macroscopic phenomenons or features of the system as we will be dealing with fundamental thermodynamic variables only. From statistical mechanics we know that any thermodynamic quantity can be derived once we know the free energy of the system. Hence, we first begin with the description of free energy in terms of our parameters.
Here the concept of order parameter plays an important role. Traditionally order parameter in Landau theory is a quantity that is zero above phase transition and non-zero below. If we consider the Curie Weiss temperature T_0 for ferroelectrics to be the critical temperature, then polarization can be considered as an order parameter. Hence we do a Taylor series expansion of F in terms of order parameter P where is F is free energy per unit volume.

$$F = \frac{aP^2}{2} + \frac{bP^4}{4} + \frac{cP^6}{6}... - EP$$

$b > 0$ for second order phase transition. Here we note that there are only even powers of P when E=0. This is due to the fact that when no electric field is applied, total spin up or spin down is the same, its just a matter of perspective! A more rigorous argument is that the Hamiltonian of the system under no external electric field condition is spin invariant i.e $H(P) = H(-P)$ and free energy is invariant too. One thing to be aware of is that,$F = 0$ when $P = 0$, we are assuming that free energy of unpolarized, unstrained crystal to be zero. Also as this is a Taylor series expansion about critical point, if we neglect higher order terms our solutions will only be accurate in the region near critical point.
In order to determine equilibrium polarization, F is minimized with respect to P. i.e

$$\frac{\partial F}{\partial P} = 0$$

which gives us the condition,

$$E = aP + bP^3 + cP^5$$

Here only three terms are being considered. Hence, we have found the equilibrium value of the electric field which can be used to derive electric susceptibility given by,

$$1/\chi = \partial E/\partial P \approx a$$

For E=0, minimizing the free energy functional and considering terms only up to fourth order, we get,

$$\partial F/\partial P = 0 = aP + bP^3$$

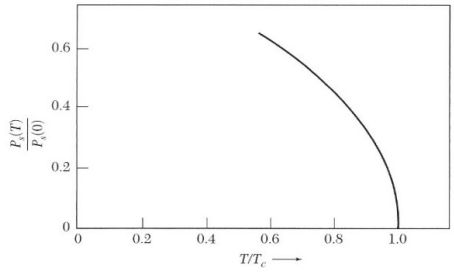
Solving for P we get,

$$P = \sqrt{\frac{-a}{b}}; T < T_0$$
$$P = 0; T >= T_0$$

A very neat trick can be employed here to get a more compact form of the above solution. This is in accordance with Curie-Weiss law which is observed in ferroelectrics for $T > T_0$ .Considering only real part of the P for all our purposes if we replace a by $a_0(T - T_0)$ we get,

$$P = \sqrt{\frac{a_0(T_0 - T)}{b}}, a_0, b > 0, T < T_0$$

If we substitute back the equilibrium value of P in the free energy functional,



This is the P vs T curve predicted theoretically, but also experimentally it was found that many ferroelectric materials follow a similar curve for e.g $BaTiO_3$

Figure 7: P vs T variation for a ferroelectric material

$$F = \frac{-a_0^2(T - T_0)^2}{4b}...$$

The relation between free energy functional and entropy of the system is,

$$S = \frac{-\partial F}{\partial T}$$

$$S = \frac{a_0^2(T - T_0)}{2b}...$$

Therefore, We can calculate latent heat L from here which is, $L = T(S_f - S_i) = 0$ This result was expected as remember we are doing this derivation for second order phase transition ($b > 0$). Later the case of $b < 0$, will be considered which will result in first order phase transition. Returning back, we know that,

$$C_v = -T\frac{\partial^2 F}{\partial T^2}$$

Hence substituting our expression of F here evaluated at $T = T_0$,

$$C_v = \frac{a_0 T_0}{2b}$$

Now coming back to reason behind $b < 0$, when $T = T_0$ there is atleast one more minima other than $P = 0$. For a tends to zero, which corresponds physically to the reduction of the temperature, this minimum will drop in energy below that of the unpolarized state, and so will be the thermodynamically favored configuration. This temperature is referred to as Curie temperature T_c which exceeds T_0. At temperature between T and T_0, upolarized state exists as local minima and at $T = T_c$ there is a discontinuity in order parameter which is a characteristic feature of first order phase transition.

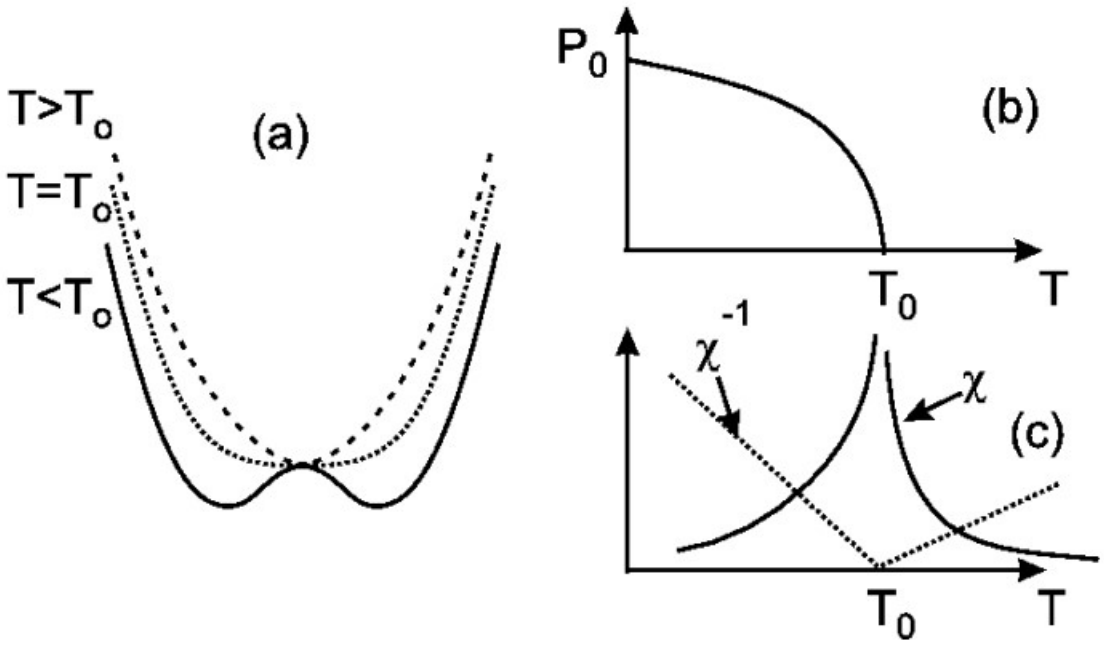


Figure 8: Plots for second order phase tranitions

So essentially at $T = T_c$, as there are equi-minima for non-zero P and $P = 0$, the state of the system depends upon how is the temperature being approached. If $T_i > T_c$, then at $T = T_c$, $P = 0$ and if $T_i < T_c$, non-zero P will be attained at $T = T_c$. We would further do a theoretical and experimental analysis of this kind of phase transition in later sections.

4 Model

To describe the phenomenon of ferroelectricity in $BaTiO_3$, we introduced the reader to the concept of Landau Theory of phase transitions and how the free energy can be expressed as a Taylor-Series expansion of the order-parameter (P) in the previous sections. Here, we will delve deeper into this model and see how it can be used to obtain the transition or Curie temperature (T_C). We start with the Landau-Devonshire potential as established previously:

$$\begin{aligned}\Delta G = \frac{1}{2}\alpha_0(T - T_0)(P_x^2 + P_y^2 + P_z^2) + \frac{1}{4}\alpha_{11}(P_x^4 + P_y^4 + P_z^4) \\ + \frac{1}{2}\alpha_{12}(P_x^2P_y^2 + P_y^2P_z^2 + P_z^2P_x^2) + \frac{1}{6}\alpha_{111}(P_x^6 + P_y^6 + P_z^6) \\ + \frac{1}{2}\alpha_{112}[P_x^4(P_z^2 + P_y^2) + P_y^4(P_x^2 + P_z^2) + P_z^4(P_x^2 + P_y^2)] + \frac{1}{2}\alpha_{123}P_x^2P_y^2P_z^2\end{aligned}$$

Now, we proceed further by differentiating ΔG with respect to the polarization parameters along different directions and equating them to 0 in order to minimize them.

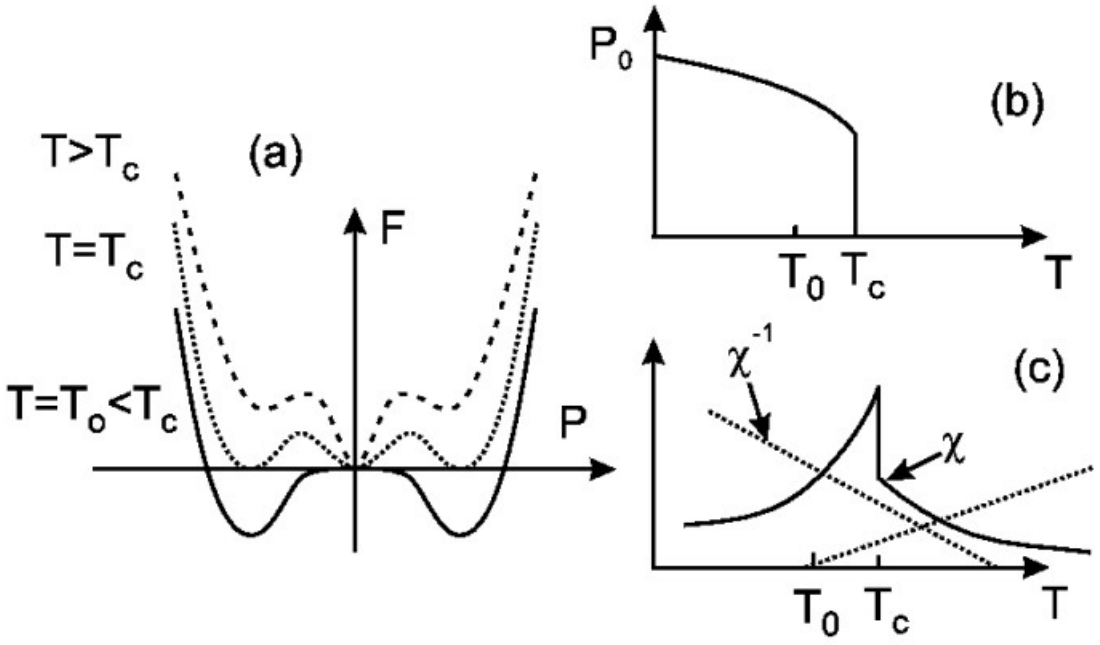


Figure 9: plots for first order phase transitions

$$F_1 = \frac{\partial \Delta G}{\partial P_x} = 0$$
$$F_2 = \frac{\partial \Delta G}{\partial P_y} = 0$$
$$F_3 = \frac{\partial \Delta G}{\partial P_z} = 0$$

Which ultimately leads us to the system of three polynomial equations that we have to solve.

$$\alpha_o(T - T_o)P_x + \alpha_{11}P_x^3 + \alpha_{12}P_x(P_y^2 + P_z^2) + \alpha_{111}P_x^5 + \alpha_{112}P_x(2P_x^2(P_y^2 + P_z^2) + P_y^4 + P_z^4) = 0$$

$$\alpha_o(T - T_o)P_y + \alpha_{11}P_y^3 + \alpha_{12}P_y(P_x^2 + P_z^2) + \alpha_{111}P_y^5 + \alpha_{112}P_y(2P_y^2(P_x^2 + P_z^2) + P_x^4 + P_z^4) = 0$$

$$\alpha_o(T - T_o)P_z + \alpha_{11}P_z^3 + \alpha_{12}P_z(P_y^2 + P_x^2) + \alpha_{111}P_z^5 + \alpha_{112}P_z(2P_z^2(P_y^2 + P_x^2) + P_y^4 + P_x^4) = 0$$

Unfortunately, this set of coupled polynomial equations is too difficult to be solved analytically, however we can solve it numerically, the details of which will be explained in the coming sections. For arguments sake, we can simplify the LD potential by considering a simplified one-dimensional case for the ferroelectric cubic-to-tetragonal phase transition.

$$\Delta G = \frac{1}{2}\alpha_o(T - T_o)P_x^2 + \frac{1}{4}\alpha_{11}P_x^4 + \frac{1}{6}\alpha_{111}P_x^6$$

Now, for such phase transitions, we have three characteristic temperatures we are interested in. The ferroelectric limit temperature (T_1), Curie temperature (T_C) and Curie-Weisse temperature (T_{CW}). Briefly, T_1 is the temperature beyond which the ferroelectric phase cannot exist, between T_C and T_1, the ferroelectric phase is meta-stable whereas the paraelectric phase is stable. And finally for between T_{CW} and T_C, the ferroelectric phase is stable and the paraelectric phase is meta-stable.
Now, we proceed to solve for T_C working on the assumption we know what the value of T_{CW} is, in the results section, we will explain how to experimentally obtain this value from the ϵ_R vs T data of the $BaTiO_3$ sample. To solve for T_C we will require the following two equations:

$$\Delta G = \frac{1}{2}\alpha_o(T - T_o)P_x^2 + \frac{1}{4}\alpha_{11}P_x^4 + \frac{1}{6}\alpha_{111}P_x^6 = 0$$
$$\frac{\partial \Delta G}{\partial P_x} = \alpha_o(T - T_o)P_x + \alpha_{11}P_x^3 + \alpha_{111}P_x^5 = 0$$

We have to solve for an expression for P_x, which we'll substitute into the expression for the minimized ΔG to obtain T_C. So we proceed by:

$$P_x(\alpha_o(T - T_o) + \alpha_{11}P_x^2 + \alpha_{111}P_x^4) = 0$$

We discard $P_x = 0$ as it's a trivial solution, we are left with a biquadratic equation, which can be reduced to a simple quadratic equation.

$$\alpha_o(T - T_o) + \alpha_{11}P_x^2 + \alpha_{111}P_x^4 = 0$$

Following which we get

$$P_x^2 = \frac{1}{2\alpha_{111}}[-\alpha_{11} \pm \sqrt{\alpha_{11}^2 - 4\alpha_o\alpha_{111}(T - T_o)}]$$

Plugging this expression back into $\Delta G = 0$, we get

$$T_C = T_o + \frac{3}{16}\frac{\alpha_{11}^2}{\alpha_o\alpha_{111}}$$

With this simplified expression for the Curie-Temperature from the one-dimensional solution to the Landau-Devonshire, we can make a good guess of the ferroelectric phase transition temperature by substituting the values of the parameters which will be done in the results section.
We can also obtain the ferroelectric limit temperature by imposing some additional constraints. At T_1 we have:

$$\alpha_{11}^2 - 4\alpha_o\alpha_{111}(T_1 - T_o) = 0$$

Which finally leads us to the expression:

$$T_1 = T_o + \frac{1}{4}\frac{\alpha_{11}^2}{\alpha_o\alpha_{111}}$$

5 Methodology

5.1 Experimental

Poly-crystalline bulk samples of $BaTiO_3$ were prepared through the standard solid-state reaction route [13] using the binary-oxide precursors Barium Oxide (BaO) and Titanium Oxide (TiO_2) powders. Stoichiometric quantities of these oxides were mixed and subsequently ground in an agate mortar for 5h, the powder was calcined at 1200^oC for 12h in air with a rising rate of 4^oC per minute and was subsequently cooled naturally. This powder was regrind for 30 minutes and then made into 13mm diameter cylindrical pellets using a hydraulic press at a pressure of 50 kg m^{-1}, following which, it was sintered at 1300^oC for 36h in air, this time with a rising rate of 5^oC per minute.
The dielectric spectroscopy measurments were taken using the impedance analyzer from NF corporation (Model No: ZM2376) coupled with the high-temperature controller and dielectric measurement chamber from SuppuSusee Instruments in the parallel-plate capacitor configuration. All Data analysis was done using OriginPro software.

5.2 Numerical

We perform numerical analysis to predict the critical temperature T_c of $BaTiO_3$ sample. We consider the below free energy expansion up to sixth order terms,

$$\begin{aligned}\Delta G = \frac{1}{2}\alpha_0(T_c - T_0)(P_x^2 + P_y^2 + P_z^2) + \frac{1}{4}\alpha_{11}(P_x^4 + P_y^4 + P_z^4) \\ + \frac{1}{2}\alpha_{12}(P_x^2P_y^2 + P_y^2P_z^2 + P_z^2P_x^2) + \frac{1}{6}\alpha_{111}(P_x^6 + P_y^6 + P_z^6) \\ + \frac{1}{2}\alpha_{112}[P_x^4(P_z^2 + P_y^2) + P_y^4(P_x^2 + P_z^2) + P_z^4(P_x^2 + P_y^2)] + \frac{1}{2}\alpha_{123}P_x^2P_y^2P_z^2\end{aligned}$$

The parameters α_0, α_{11}, α_{12}, α_{111}, α_{112}, α_{123}, T_0 were take from [11]. Our aim is to get the value of T_c for which $\Delta G = 0$. The plan is to guess a value of T_c and then minimize ΔG function with respect to P_x, P_y and P_z to get a system of three non-linear equations.

$$F_1 = \frac{\partial \Delta G}{\partial P_x} = 0$$

$$F_2 = \frac{\partial \Delta G}{\partial P_y} = 0$$

$$F_3 = \frac{\partial \Delta G}{\partial P_z} = 0$$

We use Newton-Jacobi method and Broyden's method to solve above system of equations. Although primitive, Newton-Jacobi method gave nearly same result as Broyden's method for this particular system. Hence we only consider Newton Jacobi method here on as it is more intuitive.
Newton-Jacobi method is an iterative method to get final value of the variables. Here we

assume an initial guess solution and then update our guess solution with the following procedure:

$$x^{(k)} = x^{(k-1)} - J(x^{(k-1)})^{-1} F(x^{k-1})$$

Where Jacobian (J) is given by,

$$\begin{bmatrix} \frac{\partial F_1}{\partial P_x} & \frac{\partial F_1}{\partial P_y} & \frac{\partial F_1}{\partial P_z} \\ \frac{\partial F_2}{\partial P_x} & \frac{\partial F_2}{\partial P_y} & \frac{\partial F_2}{\partial P_z} \\ \frac{\partial F_3}{\partial P_x} & \frac{\partial F_3}{\partial P_y} & \frac{\partial F_3}{\partial P_z} \end{bmatrix}$$

And $F(x)$ is,

$$\begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix}$$

A more detailed explanation of this method can be found in [12]. So building upon this method, we calculated the functions F_1, F_2, F_3 and their partial derivatives.After this we performed 100-1000 iterations to get a converging value of P_x,P_y and P_z which are substituted back in ΔG to get its value. We would like to again remind the reader that we want T_c for which ΔG tends to zero at phase transition.

6 Results

6.1 Dielectric Spectroscopy

The dielectric measurements were taken for the sample between the temperature range of 55^{o}C to 355^{o}C in order to probe and identify the cubic-to-tetragonal phase transition associated with the ferroelectric to paraelectric transition. The pellet was supplied with an ac-potential peak of 2.5V and an offset voltage of 0.5V and the temperature variation of the permittivity was measured for frequencies between 26.9 KHz and 2.37 MHz.

In the paraelectric phase region, $BaTiO_3$ obey's the Curie-Weisse law for dielectric permittivity:

$$\epsilon_R = \frac{C}{T - T_o}$$

Here, T_o is the *Curie-Weisse* Temperature, which is a statistical temperature for which the Curie-Weisse law is valid. We plot the inverse of the dielectric permittivity ($\frac{1}{\epsilon_R}$) against the temperature (T) and perform a linear fitting in the paraelectric phase region around the transition point in order to obtain the system's Curie-Weisse temperature T_o. Using this value of T_o, we substitute it into the Landau-Devonshire Potential to obtain

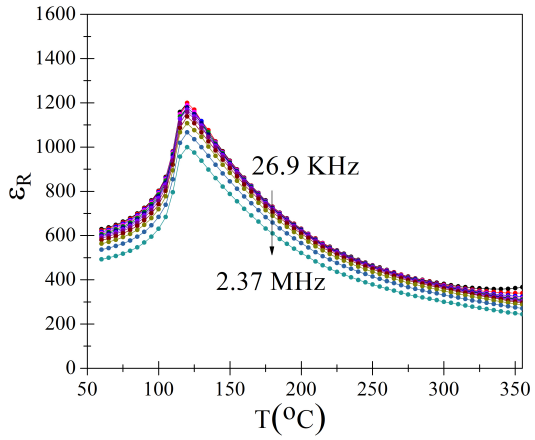
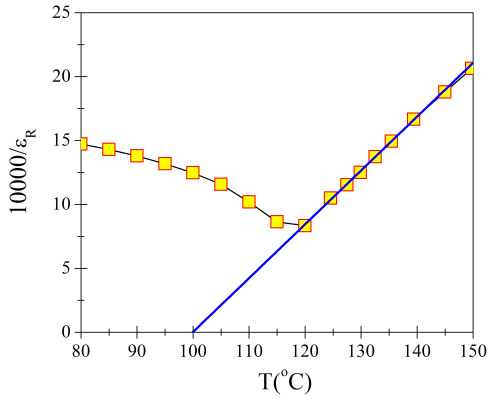


Figure 10: The ϵ_R vs T plot for the poly-crystalline $BaTiO_3$ sample

A sharp peak is observed for T $\sim$ 120^{o}C mark, which is indicative of a first-order transition as we can observe a pseudo-discontinuity beginning from around 100^{o}C . The values for the permittivity decrease with increasing frequency, indicating a sort of ferro-electric relaxor behaviour, which can also be explained using Landau's theory by incorporating additional terms into the Landau-Devonshire potential[8].

the theoretical transition temperature ($(T_C)_{LD}$) and compare it with the experimentally observed transition temperature ($(T_C)_{exp}$).

One very important thing to note for our experimental analysis is that the Curie-



The $\frac{10000}{\epsilon_R}$ vs T plot for the reduced temperature range of 80^{o}C to 150^{o}C in order to accurately determine the Curie-Weisse temperature. The linear fit was applied to the temperatures between 125^{o}C and 135^{o}C, the fitted data was subsequently extrapolated to return T_{CW}.

Figure 11: The $\frac{1}{\epsilon_R}$ vs T plot for f=26.9KHz

Temperature is not experimentally accessible, meaning that, it's signatures in the data are not obvious. The peak temperature obtained from our experimental data can be more precisely labelled as the *Ferroelectric-limit* Temperature, beyond which the ferroelectric phase disappears completely. We characterize the T_C as the temperature where the free energy of both phases is equal. Just above T_C, the ferroelectric phase is meta-stable and the paraelectric phase is stable and vice-versa for the temperature just below T_C.
The linearly fitted data returns the following parameters:

Intercept Value	Intercept Error	Slope Value	Slope Error
-42.11422	0.95748	0.42133	0.00727

The above parameters, return the temperature axis intercept $T_{CW} = 99.95 \pm 0.95021$ ^oC which will be utilized in our calculations to determine T_C from the Landau-Devonshire model.

6.2 Theoretical Results

By implementing the numerical algorithm mentioned in section 3.2, we obtain the below result

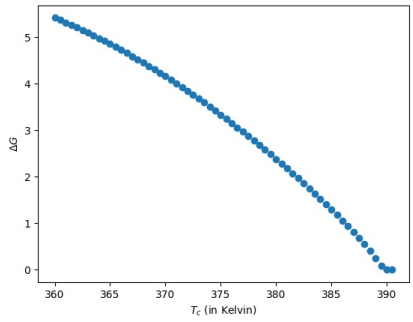


Figure 12: ΔG vs guessed T_c

The Newton-Jacobi iteration converged to a value of $(T_C)_{LD}$ of 118^oC which is remarkably close to the observed $(T_C)_{exp} \sim 120^oC$. Signifying the success of the Landau Theory of phase transitions by correlating it with the experimental data. Some deviation is to be expected as the calculations were done under ideal conditions, *i.e* Single crystalline sample, no stress or external electric field.

We observe that at around $391K$ the curve reaches zero and before that its non-zero indicating our complete set of non-linear equations are not being satisfied. Hence $T_c = 118^oC$ is our theoretically predicted value of critical temperature. The numerical program was implemented in Python as our Jacobian matrix was not very large and results were obtained in reasonable time. Github link of the source code is attached here.

a_0	3.61×10^5
T_0	373K
a_{11}	$-1.83\times10^9+4\times10^6$T
a_{111}	$1.39\times10^{10}-3.2\times10^7$T
a_{12}	$-2.24\times10^9+6.7\times10^6$T
a_{112}	-2.2×10^9
a_{123}	5.51×10^{10}

All values are in SI units

In addition to our theoretical solution, we also analytically evaluated the one-dimensional simplified equation which yielded:

$$T_C = T_o + \frac{3}{16}\frac{\alpha_{11}^2}{\alpha_o \alpha_{111}}$$

From which we obtain a value of T_C=109.61^{o}C, which, while close to the experimentally obtained temperature, is a still bit off as a result of the approximations used.

Value	1-D Theoretical	3-D Theoretical	Experimental
T_0	NA	NA	99.95^{o}C
T_C	109.61^{o}C	118^{o}C	120^{o}C

A comparison of T_C using the three methods: 1-D analytical, 3-D numerical and experimental

7 Applications

One might wonder why is there a need to study about ferroelectric materials apart from fundamental science perspective, indeed there are many applications of ferroelectrics in device physics, sensors and other domains. From the various applications we would like to focus on a very interesting application which is in memory devices.

7.1 Basics of memory device operation

One of the most simple memory device configuration is 1T1C (one transistor and one capacitor) type state. This one unit cell forms the basis of entire DRAM chip. Let us explore one bit of data is stored and retrieved in this device.

The Gate of the MOSFET device is connected to the word line and source is connected to bit line. This unit cell reads and writes data by various combinations of voltages of bit line and word line. A sense amplifier is connected to bit line which performs reading operation.
For example, when word line is high and bit line is high, the channel in MOSFET is conducting and hence capacitor is charged which typically takes nano-seconds. This charging of capacitor is equivalent to writing logic one to this unit cell. Another example would be reading voltage from the capacitor which corresponds to reading logic value. Here, the bit line is set to half of the operating voltage of the system (for e.g if system operates at 3 volts i.e logic 1 is 3 volts then 1.5 volts will be supplied to bit line) and word line is set to high. Now, if capacitor is charged, as MOSFET channel is conducting, it will discharge a little as bit line is at lower voltage, hence this excess voltage will be detected by the sense amplifier and logic 1 will be read. Similarly if capacitor is discharged initially, as bit line is high it will get a little charged, hence there will be a slight voltage decrement at bit line which will be read as logic 0 at the sense amplifier.Now billions of such 1T1C cells are connected to form a DRAM. References includes resources to learn more about this technology.

Now as MOSFET scaling is coming to an end, researchers are exploring new ferroelectric materials and mechanisms to decrease the read/write time and also increase the number of read/write cycles. One candidate which has recently again came into spotlight

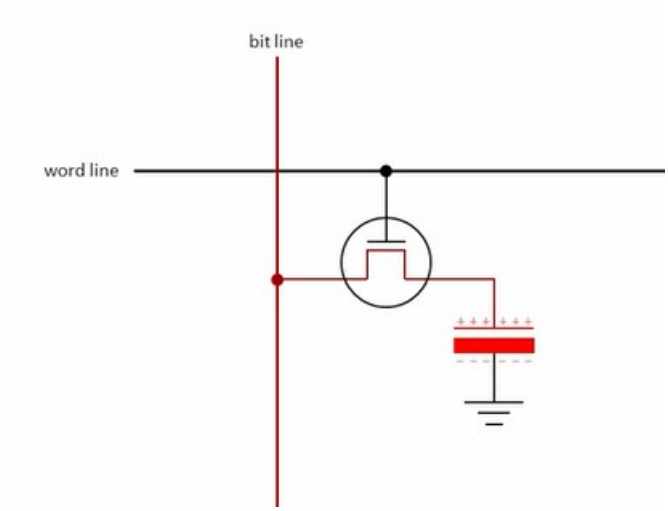


Figure 13: Circuit diagram of an 1T1C cell

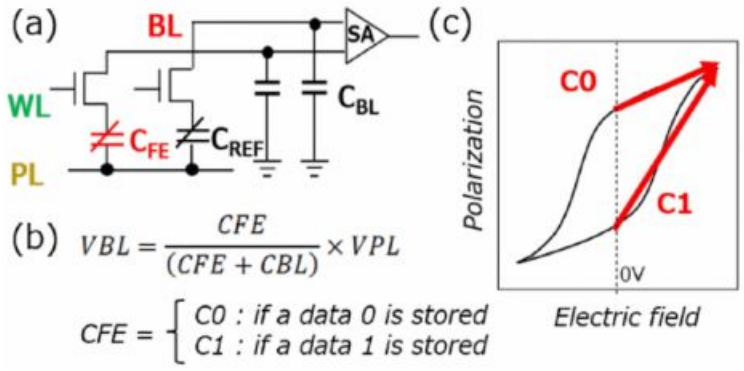


Figure 14: Experimental unit cell

is ferroelectric material Hafnium oxide which can be easily integrated in current CMOS fabrication processes. The primary idea behind using ferroelectric material as a dielectric in capacitors is its hysteresis loop property which is experimentally shown to increase the read/write time. The idea behind this is that the remnant polarization in the ferroelectric material is non-zero, hence while reading/writing later, lower time will be required to attain a complete polarization state. Also because of this property previous logic state can be detected even after it has been read (remember reading a logic state is a destructive process) which has led researchers to explore applications in neuromorphic computing, in-memory computing, etc. In order to meet to the requirements of these critical applications more theoretical and experimental studies needs to be performed to determine exact ferroelectric-paraelectric phase transition temperature, etc. as modern devices heat up a lot due to large operation per seconds so we don't want our device to stop working after a little heating or to lose data!

8 Conclusions

In conclusion, we theoretically calculated T_C from the Landau-Devonshire potential for the 1-Dimensional and 3-Dimensional using two different mathematical techniques. We employed the standard analytical method for the 1-Dimensional analysis which yielded a T_C of 109.61^{o}C and a numerical technique called the Newton-Jacobi technique for the 3-Dimensional analysis giving us a value of T_C=118^{o}C much closer to the experimentally observed value of T_C=120^{o}C. We synthesized a poly-crystalline sample of $BaTiO_3$ throught the solid-state route. We derived the relative permittivity data from the capacitance measurements of the 13 mm pellet.
Theoretically, the ferroelectric-to-paraelectric transition is a first-order transition and is supposed to show a sharp discontinuity in the ϵ_R vs T plot at T $\sim$ 120^{o}C. However, as our sample is a poly-crystalline sample, the several grains present in the pellet are their own individual crystalline *domains* per se, therefore, when we approach close to the transition temperature i.e, T $\sim$ 105^{o}C, some of the grains begin this transition before the others. In each individual grain the transition is first-order but may not appear so for the entire bulk sample.
It is due to the poly-crystalline nature of the sample, we do not observe obvious signatures of a first-order transition.
Regardless, the 3-Dimensional case for the Landau-Devonshire potential up to the 6^{th}-order returns a Curie-Temperature that is remarkably close to the observed value, signifying the success of the Landau Theory of Phase Transitions in explaining the nature the ferroelectric phase transition in $BaTiO_3$.

9 Further Research

Significant improvements can be made in this study in both the theoretical and experimental aspects.
The Landau-Devonshire potential used in the calculations was taken for an ideal case. We assumed the absence of stress and an external electric field in our potential. Some studies have shown more accurate predictions in explaining ferroelectricity by expanding the Landau-Devonshire potential up to the 8^{th}-order instead of the 6^{th}-order. Additionally, different boundary can be imposed to better theoretically explain ferroelectricity in *bulk* samples, the model we used assumes an ideal single-crystalline nature. It is due to these reasons, we observe an obvious deviation from experimental results.
Additionally, the experimental aspect of this project can be further improved on. Further studies in this direction can make efforts to produce more ideal crystalline samples such as single-crystals and impurity free. More sophisticated measurement techniques can be used to measure the dielectric permittivity such as NRW and microwave methods. Hysteresis loop measurements are required to determine the parameters α_i, α_{ij} and α_{ijk} experimentally. Using experimentally derived quantities rather than referring to literature would help in determining the accuracy of the Landau model.

10 References

References

[1] Joseph Valasek and the discovery of ferroelectricity
https://ieeexplore.ieee.org/document/522283/referencesreferences

[2] On the Phase Transitions that cannot Materialize
http://article.sapub.org/pdf/10.5923.j.ajcmp.20140401.01.pdf

[3] General phase tranition theory
https://stanford.edu/ jeffjar/statmech/week4e.html

[4] Landau theory
https://users.ox.ac.uk/ phys1116/msm-rg2.pdf

[5] Structures of the Ferroelectric Phases of Barium Titanate
https://pubs.acs.org/doi/pdf/10.1021/j100112a043?cookieSet=1

[6] A Landau Primer for Ferroelectrics
https://arxiv.org/pdf/cond-mat/0609347.pdf

[7] Landau theory of phase transitions
http://lamp.tu-graz.ac.at/ hadley/ss2/lectures16/jun20.pdf

[8] Theories and Methods of First Order Ferroelectric Phase Transitions
https://www.researchgate.net/publication/221905681

[9] A phenomenological gibbs function for BaTiO3 giving correct e field dependence of all ferroelectric phase changes
http://dx.doi.org/10.1080/00150198408240090

[10] Novel integration technologies for highly manufacturable 32 Mb FRAM
https://ieeexplore.ieee.org/document/1015456

[11] Landau expansion parameters for BaTiO3
http://wwwarchive.math.psu.edu/cao/Papers˙PDF/LuXiaoyan12-2013.pdf

[12] Numerical Methods for Solving Systems of Nonlinear Equations
https://www.lakeheadu.ca/sites/default/files/uploads/77/docs/RemaniFinal.pdf

[13] SYNTHESIS AND CHARACTERIZATION OF BaTiO3 FERROELECTRIC MATERIAL
https://inis.iaea.org/collection/NCLCollectionStore/˙Public/44/079/44079115.pdf