Intrinsic Hysteresis Loops Calculation of BZT Thin Films

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Abstract. The Landau Devonshire (LK) simulation is utilized to calculate the intrinsic hysteresis properties of Barium Zirconium Titanate (BZT) doped by Indium and Lanthanum. A Delphi program run on Windows platform is used to facilitate the calculation. The simulation is very useful to calculate and understand the Gibbs free energy and the relationship between spontaneous polarization and electric field.

Keywords. Landau Devonshire, BZT, Gibbs Energy, Hysteresis

1. Introduction
Barium Zirconium Titanate (BZT) is well known material utilized for ferroelectric devices such as FRAMs and sensor [1,2]. Therefore a theoretical consideration of the material behaviour is needed to predict its hysteresis characteristics, especially when the materials are altered by some dopants. Most of ferroelectric materials in practical applications are of first order transition, but the theoretical approach of this transition is much more complicated than the second order phase transition. Landau Devonshire (LD) is known as a static version of first order phase transition theory [3,4,6,7], it is used to understand ferroelectric phenomena such as phase transition and hysteresis properties. In this paper, the applicability of the LD equation for Barium Zirconium Titanate thin films Gibbs free energy and hysteresis loops is demonstrated. Different compositions of BZT doped by Lanthanum and Indium are compared and the ferroelectric behaviour change is analyzed.

2. Simulation
The phenomenological investigation of static properties of Barium Zirconium Titanate (BZT) are studied with the aid of Landau Devonshire (LD) equation. The LD free energy density for materials may be written [3,4]:

$$
\Delta G(P, E) = \frac{a(T - T_0)}{2\varepsilon_0} P^2 - \frac{B}{4\varepsilon_0^2} P^4 + \frac{C}{6\varepsilon_0^3} P^6 - EP
$$

where $P$ is polarization, $E$ is electric field, $T, T_0$ are temperature of sample and $a, B, C$ are constant. The permittivity $\varepsilon_0$ factor in Eq. 1 is to confirm that $a, B, C$ are simple mechanical dimensions [3]. The term in $P^6$ in eq. 1 is maintained to make dimensionless variables, hence the equation can be rewritten as:

$$
\Delta G(P, E) = \frac{1}{2} t P^2 - \frac{1}{2} P^4 + \frac{1}{6} P^6 - EP
$$

(2)
where $t$ is dimensionless variables from crystallographic data from sample. This constant ($t$) shows the phase of the materials and indicates its Gibbs free energy. One can draw the relation between the Gibbs energy as function of its polarization using the eq. 2 to get a rough idea of its behaviour. This energy is minimum, therefore:

$$ \frac{\partial \Delta G(P,E)}{\partial P} = tP - 2P^3 + P^5 - E = 0 $$

Hence the energy can be written:

$$ E = tP - 2P^3 + P^5 $$

The polarization of material can simply be written as the following:

$$ p = \sum_{i=1}^{n} q_i r_i $$

where $p$ is momen dipole, $q_i$ is atomic charge and $r_i$ is atomic radii. This equation was used to calculate momen dipole of BZT:

$$ P_s = \frac{p_{xa}}{V} $$

where $P_s$ is spontaneous polarization and $V$ is volume of crystal.

To obtain the spontaneous polarization, one should find the saddle point of the Gibbs free energy, hence the second derivative is zero. The eq. 3 becomes as the following.

$$ \frac{\partial^2 \Delta G(P,E)}{\partial P^2} = t - 6P^2 + 5P^4 = 0 $$

By solving this equation, one can obtain the spontaneous polarization as function of $t$ values [3, 8].

$$ P_s^2 = \frac{3}{5} \left( 1 + \left[ 1 - \frac{5t}{9} \right]^{1/2} \right) $$

Using spontaneous polarization of BZT calculated in the eq. 6, the value of $t$ can be obtained. These $t$ values are utilized to obtain the Gibbs energy from the LD theory. The similar scheme is also utilized to calculate the one of BZT doped by La and In. Here the calculation was on the assumption that both La and In are soft dopant where these ions have caused the raise of effective dipole moments. In this model, the interacting dopant replaces the atomic position of Ba on the crystal structure where the lattice parameters are shown in the table 1. This table also shows the complete result of dimensionless contants $t$ for BZT and BZT doped by La and In.

| Doped   | $a$     | $c$     | $V$      | $t$    |
|---------|---------|---------|----------|--------|
| BaZr$_{0.1}$Ti$_{0.9}$O$_3$ | 3.967   | 3.988   | 62.759   | 2.536  |
| 1% La   | 3.807   | 3.849   | 55.784   | 3.209  |
| 2% La   | 3.999   | 4.018   | 64.255   | 2.419  |
| 3% La   | 3.904   | 3.92    | 59.745   | 2.798  |
| 4% La   | 3.979   | 4.00    | 63.329   | 2.490  |
| 1% In   | 3.974   | 4.052   | 63.991   | 2.439  |
| 2% In   | 3.982   | 4.034   | 63.964   | 2.441  |
| 3% In   | 3.979   | 4.051   | 64.137   | 2.428  |
| 4% In   | 4.028   | 4.09    | 66.359   | 2.268  |
The hysteresis loop curves depend on the temperature difference \((T - T_0)\) or \(t\) in this case. On the extreme situation \(t\) has four conditions [4] which are \(t_{sc}\) supercooling, \(t_c\) critical temperature, \(t_{SH}\) super heating and \(t_2\) upper temperature limit of ferroelectric phase induced by electrical field.

The calculation is performed by a home made Delphi program running on Windows platform. Delphi is an objected oriented programming language as well as an integrated development environment. We have used those facilities for calculation and created graphic based routines to make it easier for visual analysis. The flowchart of the calculation is shown in the fig. 1.

![Figure 1. Simulation Method](image)

**3. Result and Discussion**

Polarization switching process and electrical field influence of BZT and BZT doped by La and In (BLZT and BIZT) thin films can be illustrated by using the LD static model. The fig. 2 shows the Gibb free energy of BZT on varying the electrical field \((e)\) at \(t: 2.536 \times 0.1\). It is clear that for positive polarization the minimum Gibbs free energy decreases on increasing the electrical field, on the contrary for negative polarization the minimum Gibbs free energy increases in the same situation. Hence, on increasing the electrical field the polarization of ferroelectric material reaches its maximum value.
Fig. 3 shows the Gibbs free energy as function of polarization for different zirconium composition. The lowest energy occurs at $x = 0.15$ composition where Ti$^{4+}$ ions replace the position of Zr$^{4+}$ ions, here we can say that the Zr$^{4+}$ ions are more stable compared with the Ti$^{4+}$ ions, this finding is in accordance with the experiment results by other authors [1,2]. Nevertheless continuously increasing the zirconium composition has caused the Gibbs free energy increases, this might be due to there is a limitation of the Zr$^{4+}$ ions that can replace Ti$^{4+}$ ions in BZT. Increasingly Zr$^{4+}$ ions within BZT causes the degree of crystalinity of BZT decreases [2].
The Gibbs free energy of BZT doped by La is shown in the fig. 4, it is clear that La doping onto BZT has caused the Gibbs free energy increases, the replacement of Ba$^{2+}$ ions by La$^{2+}$ ions has caused some damage of BZT crystal [5]. On the contrary, the situation is different for BZT doped by In, here the Gibbs free energy decreases on increasing the dopant composition. The lowest Gibbs free energy occurs at 4% Indium dopant composition.

From the grouping of ferroelectric materials, it can be seen that the value of $t$ related to the increasing electrical field could influence the stability of the phase of the material. For the values of $t > 1$, it shows the phase of material on the time of measurement is ferroelectric, based on estimation using the lattice parameter data of BZT. The calculation shows that there are slight displacement of the polarization in the fig. 6 on increasing the Zr composition. The highest polarization occurs at $x : 0.25$ zirconium composition.
When one looks closely both the fig. 2 and the fig. 6, it appears that the Gibbs free energy depends on the polarization and the electric field, meanwhile the fig. 6 itself shows that the polarization is closely related to the electric field and the hysteresis effect becomes slightly more prominent when one increases the concentration of the Zr composition. Therefore it is a clear indication that the Gibbs free energy increases on adding the Zr concentration. One should take this in a great consideration since the more Gibbs free energy of the specimen, the material becomes more unstable.

![Figure 7](image1.png)  ![Figure 8](image2.png)

**Figure 7.** Hysteresis Loops of BaZr$_{0.1}$Ti$_{0.9}$O$_3$ Doped by Lanthanum at Different Composition

**Figure 8.** Hysteresis Loops of BaZr$_{0.1}$Ti$_{0.9}$O$_3$ Doped by Indium at Different Composition

For the BZT with Zr = 0.1, the material is further doped by Lanthanum and Indium. Compared with the original property of BZT in the simulation, a similar occurrence also happens on the ferroelectric property of BZT doped by Lanthanum. The fig. 7 shows that the hysteresis loops shift on increasing the La dopant, whereas the fig. 8 shows that only a minor change arises for the case of In dopant.

In the future we will further examine the behaviour of BZT by more dopants using the calculation of dynamic model of Landau-Devonshire also known as Landau-Kalathikov (KL) model [3] to gain more understanding of its ferroelectric properties and to find the suitable dopant. Since the samples of BZT doped by In and La are already available, we would develop Sawyer Tower circuit to measure the electrical property of these materials and make a comparation with the calculated model.

### 4. Summary

From calculation using the Landau Devonshire (LD) model for BZT films, we found that lanthanum and Indium doped onto BZT have caused shifting both on the Gibbs free energy and the hysteresis curve. The lowest Gibbs free energy occurs at 4% Indium dopant composition, while the highest polarization occurs at $x : 0.25$ zirconium composition. The Simulation of the LD theory is proven workable to understand effect of dopant composition on Barium Zirconium Titanate.

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