Phase Transitions of Barium Titanate

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August 4, 2015

1 Formulation of Problem

$$\frac{\partial \Phi}{\partial u_{ij}} = 0 \rightarrow u_{ij}[P] \rightarrow \frac{\partial \Phi}{\partial P_i} = 0 \rightarrow P_i[T] \tag{1}$$

2 Strain Relations

The first derivative of the free energy gives the strain equilbrium conditions.

2.1 Tetragonal Phase

$$u_1 = -P_3^2 \frac{c_{12}q_{11} - 2c_{11}q_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{2}$$

$$u_2 = -P_3^2 \frac{c_{12}q_{11} - 2c_{11}q_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{3}$$

$$u_3 = -P_3^2 \frac{-c_{11}q_{11} - c_{12}q_{11} + 4c_{12}q_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{4}$$

$$u_4 = 0, \quad u_5 = 0, \quad u_6 = 0 \tag{5}$$

2.2 Orthorhombic Phase

$$u_1 = -P_o^2 \frac{-\frac{1}{2}c_{11}q_{11} - c_{11}q_{12} + 2c_{12}q_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{6}$$

$$u_2 = -P_o^2 \frac{c_{12}q_{11} - 2c_{11}q_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{7}$$

$$u_3 = -P_o^2 \frac{-\frac{1}{2}c_{11}q_{11} - c_{11}q_{12} + 2c_{12}q_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{8}$$

$$u_4 = 0, \quad u_5 = \frac{q_{44}P_o^2}{2c_{44}}, \quad u_6 = 0 \tag{9}$$

$$\tag{10}$$

Where $\quad P_1 = P_3 = \frac{P_o}{\sqrt{2}}$

2.3 Monoclinic Phase

$$u_1 = -\frac{P_1^2(-c_{11}q_{11} - c_{12}q_{11} + 4c_{12}q_{12}) + P_3^2(c_{12}q_{11} - 2c_{11}q_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{11}$$

$$u_2 = -\frac{P_1^2(c_{12}q_{11} - 2c_{11}q_{12}) + P_3^2(c_{12}q_{11} - 2c_{11}q_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{12}$$

$$u_3 = -\frac{P_1^2(c_{12}q_{11} - 2c_{11}q_{12}) - P_3^2(c_{11}q_{11} - c_{12}q_{11} + 4c_{12}q_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{13}$$

$$u_4 = 0, \quad u_5 = \frac{P_1 P_3 q_{44}}{c_{44}}, \quad u_6 = 0 \tag{14}$$

3 Renormalized Free Energy

Using the solutions for the strain from section 1 for each phase renormalizes the coefficients of the free energy

$$\begin{aligned} \Phi = a_1(P_1^2 + P_3^2) + a'_{11}(P_1^4 + P_3^4) + a'_{12}P_1^2P_3^2 \\ + a_{111}(P_1^6 + P_3^6) + a_{112}P_1^2P_3^2(P_1^2 + P_3^2) \end{aligned} \tag{15}$$

Where the renormalized coefficients $a'_{11}$and a'_{12} are determined by the strain relation found in the previous section.

3.1 Renormalized Parameters

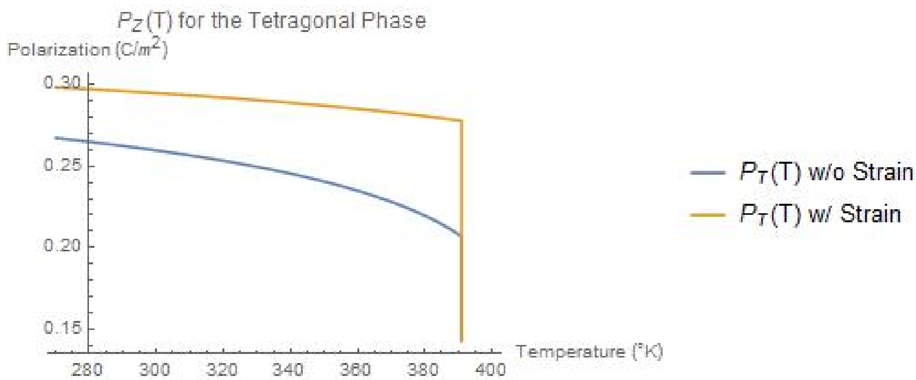
$$a'_{11} = -\frac{-2a_{11}\left(c_{11}^2 + c_{12}c_{11} - 2c_{12}^2\right) + c_{12}q_{11}\left(q_{11} - 8q_{12}\right) + c_{11}\left(q_{11}^2 + 8q_{12}^2\right)}{2\left(c_{11} - c_{12}\right)\left(c_{11} + 2c_{12}\right)} \tag{16}$$

$$a'_{12} = \frac{\begin{gathered}2a_{12}\left(c_{11}^2 + c_{12}c_{11} - 2c_{12}^2\right)c_{44} + 2c_{12}^2q_{44}^2 \\ - c_{11}\left(c_{11}q_{44}^2 + 8c_{44}q_{12}\left(q_{11} + q_{12}\right)\right) + c_{12}\left(2c_{44}\left(q_{11}^2 + 8q_{12}^2\right) - c_{11}q_{44}^2\right)\end{gathered}}{2\left(c_{11} - c_{12}\right)\left(c_{11} + 2c_{12}\right)c_{44}} \tag{17}$$

4 Equilibrium Polarization

4.1 Tetragonal Polarization

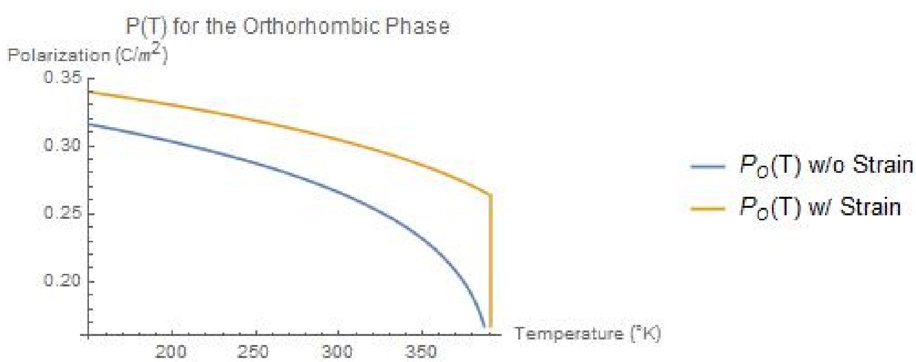
$$P_3 = \sqrt{\frac{\sqrt{(a'_{11})^2 - 3a_1 a_{111}} - a'_{11}}{3a_{111}}} \tag{18}$$



4.2 Orthorhombic Polarization

The Orthorhombic polarization vector is aligned in the (101) plane:

$$P_1 = P_3 = \sqrt{\frac{\sqrt{(2a'_{11} + a'_{12})^2 - 12a_1\left(a_{111} + a_{112}\right)} - 2a'_{11} - a'_{12}}{6(a_{111} + a_{112})}} \tag{19}$$



4.3 Monoclinic (M_C) Polarization

The Monoclinic polarization vector is aligned in the same (101) plane as in the Orthorhombic phase but with unequal components

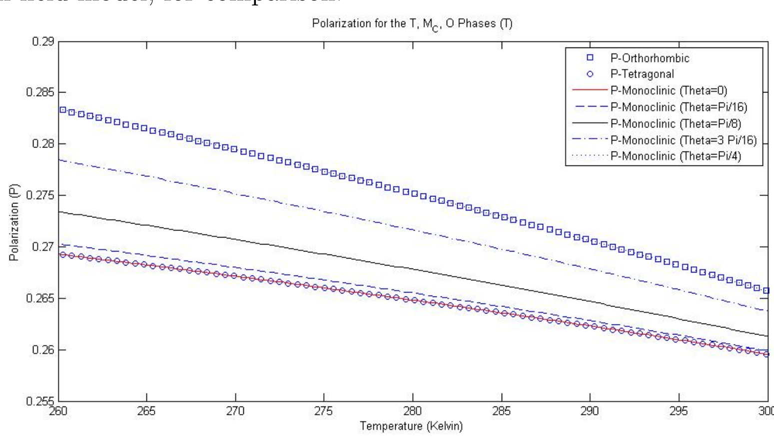
$$P_1 = \frac{\sqrt{\frac{\mp B + C}{(a_{112} - 3a_{111})^2}}}{\sqrt{2}} \tag{20}$$

$$P_3 = \frac{\sqrt{\frac{\pm B + C}{3a_{111} - a_{112}}}}{\sqrt{6a_{111} - 2a_{112}}} \tag{21}$$

$$B = \sqrt{3a_{111} - a_{112}}[3a_{111}\left(8a_1 a_{112} + 4(a'_{11})^2 + 4a'_{11}a'_{12} - 3(a'_{12})^2\right) - a_{112}\left(4a_1 a_{112} + 20(a'_{11})^2 - 12a'_{11}a'_{12} + (a'_{12})^2\right) - 36a_1 a_{111}^2]^{1/2} \tag{22}$$

$$C = a_{111}(3a'_{12} - 6a'_{11}) + 2a_{112}a'_{11} - a_{112}a'_{12} \tag{23}$$

Equation was determined using the phenomenological study of the elastic field detailed in section 2; however, since the monoclinic phase in barium titanate has been a recent observation the elastic constants are yet unknown. Disregarding the elastic field a numerical approximation can analyzed graphically and is given in the figure shown. Theta in the figure describes the angle of the polarization vector in the (101) plane. The polarization solutions for the T and O phases are given for reference, with the solutions being independent of the strain field model, for comparison.



5 Strain as a Function of Temperature

5.1 Tetragonal Strain

For the Tetragonal Phase we have:

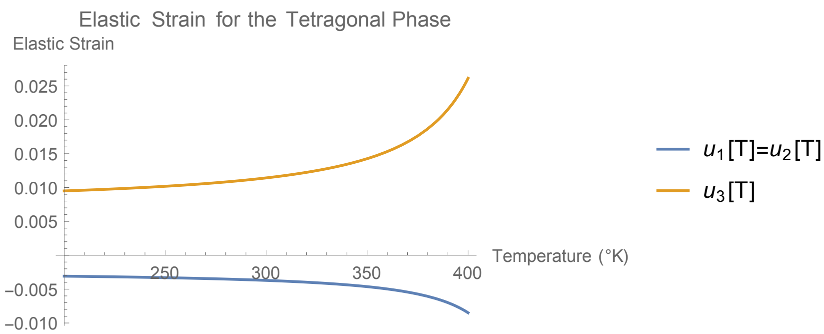
$$u_1 = \frac{\left(\sqrt{(a'_{11})^2 - 3a_1 a_{111}} - a'_{11}\right)(2c_{11}q_{12} - c_{12}q_{11})}{3a_{111}(c_{11} - c_{12})(c_{11} + 2c_{12})}, \tag{24}$$

$$u_2 = \frac{\left(\sqrt{(a'_{11})^2 - 3a_1 a_{111}} - a'_{11}\right)(2c_{11}q_{12} - c_{12}q_{11})}{3a_{111}(c_{11} - c_{12})(c_{11} + 2c_{12})}, \tag{25}$$

$$u_3 = \frac{\left(\sqrt{(a'_{11})^2 - 3a_1 a_{111}} - a'_{11}\right)(c_{11}q_{11} + c_{12}(q_{11} - 4q_{12}))}{3a_{111}(c_{11} - c_{12})(c_{11} + 2c_{12})}, \tag{26}$$

$$u_4 = 0, \quad u_5 = 0, \quad u_6 = 0 \tag{27}$$

Out[1755]=



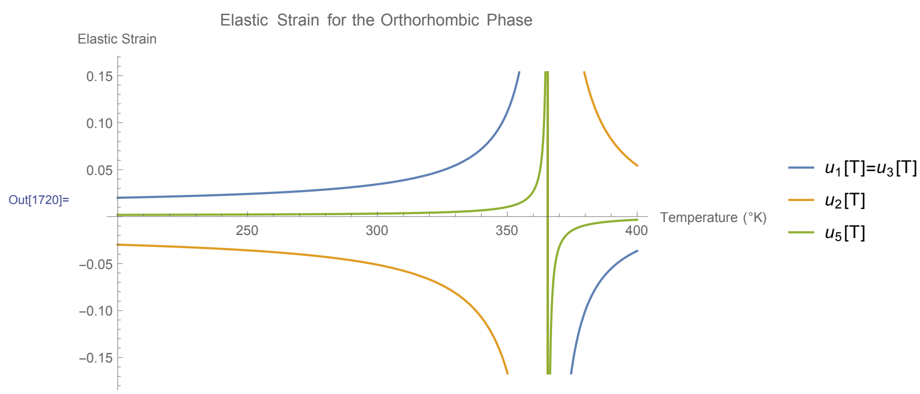
5.2 Orthorhombic Strain

$$u_1 = \frac{\left(-2a'_{11} - a'_{12} + \sqrt{(2a'_{11} + a'_{12})^2 - 12a_1(a_{111} + a_{112})}\right)(c_{11}(q_{11} + 2q_{12}) - 4c_{12}q_{12})}{12(a_{111} + a_{112})(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{28}$$

$$u_2 = \frac{\left(-2a'_{11} - a'_{12} + \sqrt{(2a'_{11} + a'_{12})^2 - 12a_1(a_{111} + a_{112})}\right)(2c_{11}q_{12} - c_{12}q_{11})}{6(a_{111} + a_{112})(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{29}$$

$$u_3 = \frac{\left(-2a'_{11} - a'_{12} + \sqrt{(2a'_{11} + a'_{12})^2 - 12a_1(a_{111} + a_{112})}\right)(c_{11}(q_{11} + 2q_{12}) - 4c_{12}q_{12})}{12(a_{111} + a_{112})(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{30}$$

$$u_4 = 0, \quad u_5 = \frac{q_{44}\left(-2a'_{11} - a'_{12} + \sqrt{(2a'_{11} + a'_{12})^2 - 12a_1(a_{111} + a_{112})}\right)}{12(a_{111} + a_{112})c_{44}}, \quad u_6 = 0 \tag{31}$$



5.3 Monoclinic Strain