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Gyrotropic and piezoelectric coefficients and attenuation of elastic waves in $BaTiO_3$

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Abstract. Using Landau theory of phase transition, expressions for gyrotropic coefficients and piezoelectric coefficients are obtained for barium titanate in the tetragonal phase. Both coefficients vanish at the ferroelectric phase transition temperature. The piezoelectric coefficients tallied with the literature values. The attenuation coefficients for elastic waves propagating along the principal directions in tetragonal, orthorhombic and rhombohedral phases are derived based on Landau theory. It is predicted that there will be slight amplification for both longitudinal and transverse modes in the rhombohedral phase at a temperature close to the rhombohedral phase transition temperature.

Keywords. Gyrotropic and piezoelectric coefficients; attenuation; elastic waves; phase transition.

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1. Introduction

Barium titanate is a classical example of a substance undergoing a first order phase transition. It is paraelectric above Curie temperature (T_c), 120 °C, and has a cubic perovskite structure. At the Curie point the structure changes from cubic m3m (O_h) to tetragonal 4 mm (C_{4V}) with spontaneous polarization (SP) along (001) direction. Below 5 °C the SP points in the (011) direction and the crystal system is orthorhombic 2 mm (C_{2V}). On cooling below -70 °C it undergoes a further phase transition to rhombohedral 3 m (C_{3V}) with SP along (111) direction.

Considering the tetragonal, orthorhombic and rhombohedral phases as strained forms of cubic phase the author obtained expressions for elastic anomalies [1–3] using Landau theory of phase transitions. Using the second order elastic anomalies already published [1–3] expressions for the gyrotropic and piezoelectric coefficients for the barium titanate in the tetragonal phase are derived. Expressions are also obtained for the attenuation of elastic waves travelling along the principal directions (100), (110) and (111).

2. Gyrotropic coefficients

When spatial dispersion is present in a system the elastic constant matrix [4] acquires the structure.

$$C_{ij}(\Omega, \mathbf{k}) = C_{ij}(\Omega) + id_{ijl}(\Omega, \mathbf{k})\mathbf{k}_1 \tag{1}$$

where $\mathbf{k}$ denotes the wave vector of the acoustic wave, Ω its circular frequency. d_{ijl} are gyrotropic tensor components (5th rank). Their number depends on the crystal system and these have been worked out by Kumaraswamy and Krishnamurthy [4].

The free energy F of the crystal can be written as the sum of (i) elastic energy F_{ela} (ii) the Landau energy F_L (iii) the energy due to coupling between order parameter (in this case SP) and strains F_c (iv) the gyrotropic energy involving SP and elastic strains and also the spatial derivatives of SP and those of strains F_g.

$$F = F_{\mathrm{ela}} + F_L + F_c + F_g \tag{2}$$

Since the term F_g is usually much smaller than F_c it can be neglected in the calculation of elastic anomalies and F_g should be taken into account while estimating gyrotropic coefficients. The expressions for F_{ela}, F_L and F_c are given in earlier publications on barium titanate [1–3].

F_g is chosen as equal to

$$\begin{aligned}
&B_1[(P_x(\partial\eta_1/\partial x) + P_y(\partial\eta_2/\partial y)) - (\eta_1(\partial P_x/\partial x) + \eta_2(\partial P_y/\partial y))]\\
&+ B_2[(P_x(\partial\eta_2/\partial x) + P_y(\partial\eta_1/\partial y)) - (\eta_2(\partial P_x/\partial x) + \eta_1(\partial P_y/\partial y))]\\
&+ B_3[(P_x(\partial\eta_5/\partial z) + P_y(\partial\eta_4/\partial z)) - (\eta_5(\partial P_x/\partial z) + \eta_4(\partial P_y/\partial z)]\\
&+ B_4[(P_x(\partial\eta_3/\partial x) + P_y(\partial\eta_3/\partial y)) - (\eta_3(\partial P_x/\partial x) + \eta_3(\partial P_y/\partial y))]\\
&+ B_5[(P_x(\partial\eta_6/\partial y) + P_y(\partial\eta_6/\partial x)) - (\eta_6(\partial P_x/\partial y) + \eta_6(\partial P_y/\partial x))]\\
&+ B_6[(P_z(\partial\eta_1/\partial z) + P_z(\partial\eta_2/\partial z)) - (\eta_1(\partial P_z/\partial z) + \eta_2(\partial P_z/\partial z))]\\
&+ B_7[P_z(\partial\eta_3/\partial z) - \eta_3(\partial p_z/\partial z)]\\
&+ B_8[(P_z(\partial\eta_5/\partial x) + P_z(\partial\eta_4/\partial y)) - (\eta_5(\partial P_z/\partial x) + \eta_4(\partial P_z/\partial y))]
\end{aligned} \tag{3}$$

where $B_i (i = 1$ to $8)$, $\eta_i (i = 1$ to $6)$ and $P_K (K = x, y, z)$ are constants, strains and components of SP respectively. F_g is chosen so that it is invariant under the transformation of the generating matrices of the tetragonal group 4 mm (C_{4V}). Each term in the square brackets in the expression for F_g given above is a difference of two terms which are individually invariant under the symmetry operations of the tetragonal groups. It is also necessary to choose equal but opposite coefficients (Bi's) for the two terms. This was warranted by the fact that the gyrotropic coefficients d_{ijl} must change sign [4] for any interchange of indices i and j. The following relations for the equilibrium values of the components of SP and their fluctuations for the tetragonal phase are taken from the earlier publications [1, 2].

$$P_{x0}^2 = P_{y0}^2 = 0 \tag{4}$$

$$P_{z0}^2 = -aP = 0{\cdot}284 \times 10^{12} a. \tag{5}$$

$$P_x^* = A\eta_5^* \tag{6}$$

$$P_y^* = A\eta_4^* \tag{7}$$

$$P_z^* = \sum_{i=1}^{6} \alpha_i \eta_i^* \tag{8}$$

where $a = a'(T - T_c)$ with a' a positive constant. P is a constant and η_i^* ($i = 1$ to 6) are fluctuations in strains about their equilibrium values.

$$A = -(\Gamma_1 g_{44} P_{z0})/P_1 = \frac{0{\cdot}502 \times 10^6}{\sqrt{a}(1 + i\Omega\pi)} \tag{9}$$

$$\alpha_1 = \alpha_2 = -(2\Gamma_3 g_{12} P_{z0})/P_3 = \frac{-0{\cdot}0227 \times 10^6}{\sqrt{a}(1 + i\Omega\tau)} \tag{10}$$

$$\alpha_3 = -(2\Gamma_3 g_{11} P_{z0})/P_3 = \frac{0{\cdot}320 \times 10^6}{\sqrt{a}(1 + i\Omega\tau)} \tag{11}$$

$$\alpha_4 = \alpha_5 = \alpha_6 = 0 \tag{12}$$

$$P_1 = \Gamma_1 8{\cdot}5a(1 + i\Omega\tau) \tag{13}$$

$$P_3 = \Gamma_3 37{\cdot}5a(1 + i\Omega\tau). \tag{14}$$

The relaxation time τ is defined as

$$\tau = \Gamma_j \left(\frac{\partial^2 F}{\partial P_K^2}\right)_0 \quad j = 1 \text{ to } 3 \quad \text{and} \quad K = x, y, z \tag{15}$$

The numerical values for P, A, $\alpha_1 = \alpha_2$, and α_3 are calculated using the values of elastic constants, g_{11}, g_{12} and g_{44} taken from Devonshire [5].

The cubic phase has inversion symmetry, hence all the d_{ijl} are zero in this phase. In the tetragonal phase d_{ijl} arises due to the absence of the inversion symmetry. By substituting $P_K = P_{K0} + P_K^*$ and $\eta_i = \eta_{i0} + \eta_i^*$ in the expression for F_g the gyrotropic coefficients are given by [6]

$$d_{ijl} = \frac{\partial^2 F}{\partial \eta_i^* (\partial \eta_j^* / \partial x_1)}. \tag{16}$$

The following gyrotropic coefficients can be obtained with the relations among them.

$$d_{133} = d_{233} = B_7 \alpha_1 = -\frac{B_7 0{\cdot}0227}{\sqrt{a}(1 + i\Omega\tau)} \times 10^6 \tag{17}$$

$$d_{142} = d_{251} = B_8 \alpha_1 = -\frac{B_8 0{\cdot}0227}{\sqrt{a}(1 + i\Omega\tau)} \times 10^6 \tag{18}$$

$$d_{151} = d_{242} = B_8 \alpha_1 = -\frac{B_8 0{\cdot}0227}{\sqrt{a}(1 + i\Omega\tau)} \times 10^6 \tag{19}$$

$$d_{342} = d_{351} = B_8 \alpha_3 = \frac{B_8 0{\cdot}320}{\sqrt{a}(1 + i\Omega\tau)} \times 10^6 \tag{20}$$

$$d_{461} = d_{562} = B_5 A = \frac{B_5 0{\cdot}502}{\sqrt{a}(1 + i\Omega\tau)} \times 10^6 \tag{21}$$

All the above five independent gyrotropic coefficients appropriate to C_{4V} are listed by Kumaraswamy and Krishnamurthy [4]. The coefficients are complex and proportional to $[(T - T_c)^{1/2}(1 + i\Omega\tau)]^{-1}$. The temperature variation of τ is given by Lemanov [7]

$$\tau = \frac{\tau_0}{|T - T_c|} \tag{22}$$

with $\tau_0 = 10^{-11}$ sk. For numerical calculations the experimental value of Ω is chosen as equal to $10^9\,s^{-1}$. The real part of the coefficients follows the variation of the term $(T - T_c)^{3/2}[(T - T_c)^2 + \Omega^2\tau_0^2]^{-1}$. At $T = T_c$ all the coefficients vanish. For $T - T_c = \Omega\tau_0 = 10^{-2}$ the coefficients are proportional to 10^5 to 10^6.

3. Piezoelectric coefficients

When the free energy is expressed in terms of strains and electric field, one obtains piezoelectric stress coefficients e_{mi} [8]. If free energy is expressed in terms of stresses and electric field, piezoelectric strain coefficients d_{mi} will result [8]. Using polarization theory and by replacing electric field with polarization in the expression for free energy one can also get the a and b coefficients (a_{mi} and b_{mi}) as referred to by Cady [8].

The expression for the first thermodynamic potential is given by

$$\xi = 1/2C_{ij}^P\eta_i\eta_j + 1/2\chi_{km}^s P_K P_m + a_{mi}P_m\eta_i \quad (23)$$

where C_{ij}^P are elastic constants at constant polarization, χ_{km}^s are inverse susceptibilities at constant strain (clamped constants or high frequency values) P_K are components of polarization and η_i are strains. By introducing $P_K = P_{K0} + P_K^*$ and $\eta_i = \eta_{i0} + \eta_i^*$ in the expression for free energy $F = F_{ela} + F_L + F_c$ and comparing it with (23) the piezoelectric coefficients a_{mi} are the coefficients of $P_K^*\eta_i^*$. For the tetragonal phase of barium titanate they are listed with their numerical values as

$$a_{33} = 2g_{11}P_{z0} = -11{\cdot}94\sqrt{a'(T - T_c)} \times 10^6 \quad (24)$$

$$a_{32} = 2g_{12}P_{z0} = +0{\cdot}85\sqrt{a'(T - T_c)} \times 10^6 \quad (25)$$

$$a_{15} = a_{24} = g_{44}P_{20} = -4{\cdot}26\sqrt{a'(T - T_c)} \times 10^6. \quad (26)$$

Devonshire [9] derived the following relations between C_{ij}^P, a_{mi}, b_{mi} and η_{mn}^T (susceptibilities at constant stress) as

$$a_{mi} = b_{mj}C_{ji}^P \quad (27)$$

$$d_{mi} = b_{ni}\eta_{mn}^T \quad (28)$$

The values of d_{mi} are of the order 10^{-6} C_{ji}^P's are of the order 10^{12}, b_{mi} are of the order 10^{-7} and η_{mn}^T are of the order 10 to 100. The piezoelectric constants calculated by the author from Landau theory are of the order 10^6 and tally with the reported values. The coefficients a_{33}, a_{32} and a_{15} vanish at $T = T_c$ and they vary as $\sqrt{T - T_c}$.

4. Attenuation

Lemanov obtained an expression for the attenuation coefficient (α) in terms of real and imaginary parts of the elastic constants [7] as

$$\alpha = (\Omega/2)\mathrm{Im}aC_{ij}/\mathrm{Re}\,C_{ij} \quad (29)$$

The elastic anomalies reported by the author in different phases of barium titanate are complex [1–3]. Using (29) expressions for the attenuation coefficients (α's) can be written in terms of $\Omega\tau = x$ for the longitudinal and transverse waves along the principal directions in tetragonal, orthorhombic and rhombohedral phases of barium titanate

Tetragonal

(100)

$$\alpha_{l_1} = \frac{0{\cdot}971x^3}{(1+x^2)^2} \times 10^8 \tag{30a}$$

$$\alpha_{t_1} = \frac{15{\cdot}873x^3}{(1+x^2)^2} \times 10^8 \tag{30b}$$

(110)

$$\alpha_{l_{11}} = \frac{6{\cdot}756x^3}{(1+x^2)^2} \times 10^8 \tag{31a}$$

$$\alpha_{t_{11}} = 0 \tag{31b}$$

(111)

$$\alpha_{l_{111}} = \frac{8{\cdot}141x^3}{(1+x^2)^2} \times 10^8 \tag{32}$$

$$\alpha_{t_{111}} = \frac{10{\cdot}417x^3}{(1+x^2)^2} \times 10^8 \tag{32b}$$

Orthorhombic

(100)

$$\alpha_{l_1} = \frac{x(0{\cdot}03 + 0{\cdot}02x^2)}{(0{\cdot}81 + x^2)^2} 4{\cdot}854 \times 10^8 \tag{33a}$$

$$\alpha_{t_1} = \frac{x(0{\cdot}85 + 0{\cdot}6x^2)}{(0{\cdot}81 + x^2)^2} 7{\cdot}937 \times 10^8 \tag{33b}$$

(110)

$$\alpha_{l_{11}} = \frac{x(0{\cdot}83 + 0{\cdot}75x^2)}{(0{\cdot}81 + x^2)^2} 1{\cdot}672 \times 10^8 \tag{34a}$$

$$\alpha_{t_{11}} = \frac{x(0{\cdot}93 + 0{\cdot}52x^2)}{(0{\cdot}81 + x^2)^2} 15{\cdot}152 \times 10^8 \tag{34b}$$

(111)

$$\alpha_{l_{111}} = \frac{x(1{\cdot}63 + 1{\cdot}48x^2)}{(0{\cdot}81 + x^2)^2} 1{\cdot}010 \times 10^8 \tag{35a}$$

$$\alpha_{t_{111}} = \frac{x(1{\cdot}78 + 1{\cdot}14x^2)}{(0{\cdot}81 + x^2)^2} 5{\cdot}208 \times 10^8 \tag{35b}$$

Rhombohedral

(100)

$$\alpha_{l_1} = \frac{x(-0{\cdot}21 + 3{\cdot}93x^2 + 9{\cdot}63x^4 + 6{\cdot}14x^6)}{(1 + 2{\cdot}6x^2 + 1{\cdot}44x^4)^2} 4{\cdot}854 \times 10^8 \tag{36a}$$

$$\alpha_{t_1} = \frac{x(-0{\cdot}15 + 1{\cdot}87x^2 + 3{\cdot}47x^4 + 1{\cdot}73x^6)}{(1 + 2{\cdot}6x^2 + 1{\cdot}44x^4)^2} 7{\cdot}937 \times 10^8 \quad (36b)$$

(110)

$$\alpha_{1_{11}} = \frac{x(-0{\cdot}45 + 8{\cdot}53x^2 + 17{\cdot}35x^4 + 8{\cdot}81x^6)}{(1 + 2{\cdot}6x^2 + 1{\cdot}44x^4)^2} 1{\cdot}672 \times 10^8 \quad (37a)$$

$$\alpha_{t_{11}} = \frac{x(-0{\cdot}26 + 3{\cdot}07x^2 + 8{\cdot}84x^4 + 6{\cdot}90x^6)}{(1 + 2{\cdot}6x^2 + 1{\cdot}44x^4)^2} 15{\cdot}152 \times 10^8 \quad (37b)$$

(111)

$$\alpha_{1_{111}} = \frac{x(-0{\cdot}7 + 13{\cdot}13x^2 + 25{\cdot}1x^4 + 11{\cdot}5x^6)}{(1 + 2{\cdot}6x^2 + 1{\cdot}44x^4)^2} 1{\cdot}010 \times 10^8 \quad (38a)$$

$$\alpha_{t_{111}} = \frac{x(-0{\cdot}41 + 4{\cdot}94x^2 + 12{\cdot}3x^4 + 8{\cdot}64x^6)}{(1 + 2{\cdot}6x^2 + 1{\cdot}44x^4)^2} 5{\cdot}208 \times 10^8 \quad (38b)$$

The variation of attenuation coefficients with $\Omega\tau = x$ along the principal directions in the three phases are illustrated in figures (1a, b and c). The following observations can be inferred from the curves. 1) The attenuation is maximum for the rhombohedral phase for the transverse mode along (110) direction. 2) Attenuation is minimum for the tetragonal phase for the longitudinal mode along (100) direction and vanishes for the transverse mode along (110) direction. 3) In the case of tetragonal and rhombohedral phases maximum attenuation occurs around $\Omega\tau = 1{\cdot}75$ which corresponds to $(T - T_c) \simeq 10^{-3}$ K 4) For the orthorhombic phase maximum attenuation occurs around $\Omega\tau = 0{\cdot}75$ corresponding to $(T - T_c) \simeq 10^{-2}$ K. 5) Landau theory predicts for both modes in rhombohedral phase slight amplification for $\Omega\tau$ between 0 to 0·2 with

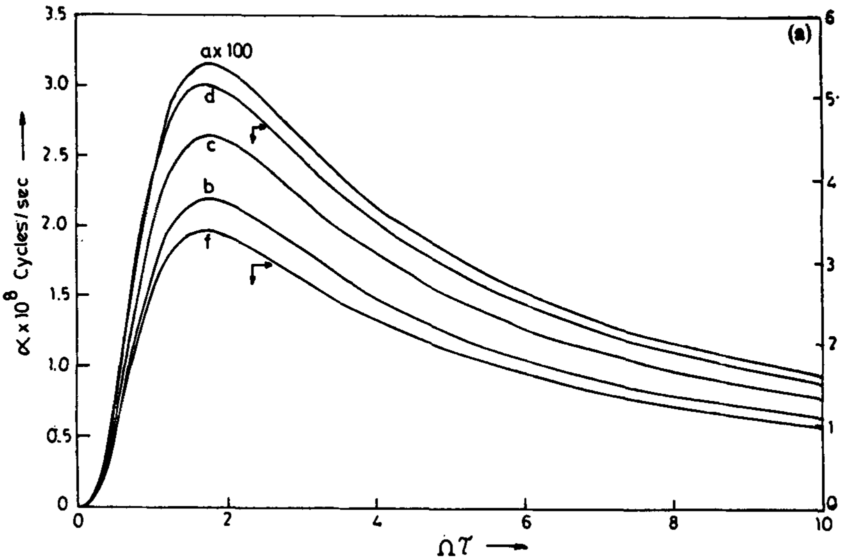
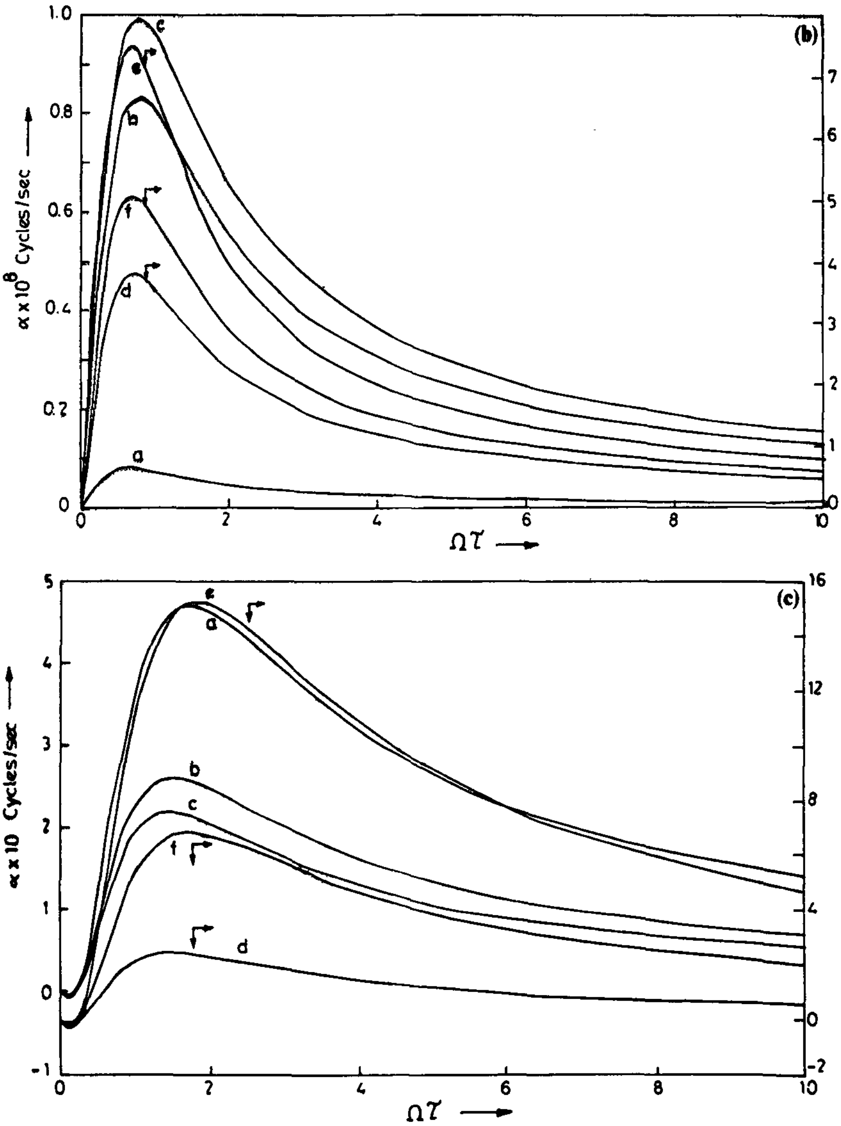


Figure 1. *(Continued)*



Figures 1(a)–(c). Represent variation of attenuation coefficients with the product of circular frequency and relaxation time ($\Omega\tau$) in tetragonal, orthorhombic and rhombohedral phases respectively. In each figure curve (a) α_{l_1} (b) $\alpha_{l_{11}}$ and (c) $\alpha_{l_{111}}$ represent attenuation coefficients of longitudinal mode along (100), (110) and (111) directions respectively. Curve (d) α_{t_1}, (e) $\alpha_{t_{11}}$ and (f) $\alpha_{t_{111}}$ represent attenuation coefficients of transverse mode along (100), (110) and (111) directions respectively.

maximum amplification for $\Omega\tau = 0{\cdot}1$ which corresponds to $(T - T_c) \simeq 0{\cdot}1$ K. Unfortunately, there are no experimental data available for comparison. It is hoped that the present work will stimulate experimental investigations to prove the validity of the theoretical predictions.

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