Critical behavior of the spontaneous polarization and the dielectric susceptibility close to the cubic-tetragonal transition in BaTiO$_3$

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Using Landau mean field model, the spontaneous polarization and the dielectric susceptibility are analyzed as functions of temperature and pressure close to the cubic–tetragonal (ferroelectric–paraelectric) transition in BaTiO$_3$. From the analysis of the dielectric susceptibility and the spontaneous polarization, the critical exponents are deduced in the classical and quantum limits for BaTiO$_3$. From the critical behavior of the dielectric susceptibility, the spontaneous polarization can be described for the ferroelectric–paraelectric (cubic to tetragonal) transition between 4 and 8 GPa at constant temperatures of 0 to 200 K in BaTiO$_3$ within the Landau mean field model given here.

Keywords: Dielectric susceptibility; spontaneous polarization; ferroelectric–paraelectric transition; Landau mean field model; BaTiO$_3$.

1. Introduction

The dielectric properties of BaTiO$_3$ as a well-known ferroelectric material$^1$ have been studied at various hydrostatic pressures and temperatures.$^2$ It exhibits successive transitions between cubic and tetragonal (C–T) phases (paraelectric–ferroelectric), between tetragonal and orthorhombic (T–O) phases (ferroelectric–ferroelectric) and between orthorhombic–rhombohedral (O–R) phases (ferroelectric–paraelectric) which have been studied experimentally, as shown in the T–P phase diagrams.$^2,3$ From the dielectric study of BaTiO$_3$, it was found that the cubic–tetragonal (C–T) transition temperature in particular decreased linearly with pressure in the range of 1 bar to 3 GPa, as also pointed out previously.$^3$ Above 3 GPa, there occurs the critical point at which the first- and second-order transitions cross over as suggested in an earlier study.$^2$ For the hexagonal–orthorhombic (H–O) phase transition in hexagonal BaTiO$_3$ ($h$-BaTiO$_3$), the critical pressure was obtained as 3.4 GPa.$^4$ Its specific heat can be compared with that of perovskite BaTiO$_3$ ($p$-BaTiO$_3$) with a similar Debye temperature,$^2$ as also pointed out previously.$^3$ At room temperature, BaTiO$_3$ has a tetragonal perovskite structure with the point group $C_{4v}$. As the temperature increases up to the Curie temperature (~ 400 K), it undergoes the cubic phase with the point group $O_h$. The Raman spectroscopy has been used to investigate the tetragonal phase in BaTiO$_3$ in some earlier studies.$^6–9$ Studies on infrared reflectivity,$^10$ Raman$^{10,11}$ and light scattering$^{12}$ have focused on the soft modes in BaTiO$_3$.

Thin films of barium titanate using X-ray diffraction$^{13}$ and Raman spectroscopy$^{13,14}$ have been studied to investigate the ferroelectric–paraelectric transition. Recently, ferroelectric transition in barium titanate nanoparticles has been studied using NMR spectra.$^{15}$ We have also studied soft modes in ferroelectric$^{16}$ and hexagonal BaTiO$_3$.$^{17}$ We have calculated the damping constant for the tetragonal Raman mode of BaTiO$_3$. $^{18}$

In regard to the dielectric properties of barium titanate, continued existence of a permanent polarization above the Curie temperature was reported many years ago and above $120^\circ$, the dielectric susceptibility obeys the Curie–Weiss law,$^{19}$ as also studied in the cubic paraelectric phase of this material.$^2$ It has been reported that porosity and pore size effect on the dielectric properties of BaTiO$_3$ ceramic and that the dielectric susceptibility decreases abruptly as the porosity increases.$^{20}$ It has also been observed experimentally that the dielectric susceptibility increased with increasing the amount of dopant for Ba$_{1−x}$Ce$_x$TiO$_3$ compounds.$^{21}$

In order to investigate the temperature and pressure dependence of the dielectric constant (dielectric susceptibility) and the spontaneous polarization close to the phase transitions in BaTiO$_3$, the Landau mean field models have been employed.$^{12,13,15}$ By expanding the free energy in terms of
the order parameter (spontaneous polarization \( P \)), the
temperature dependence of the \( P \) and the dielectric susceptibility
\( \chi \) (dielectric constant \( \varepsilon \)) can be obtained by determining
the coefficients in the free energy expansion. The temperature
dependence of the bilinear coupling constant (order parameter)
of the soft-optic and acoustic mode in hexagonal barium
titanate has been analyzed using the experimental data\(^{12}\)
according to the prediction of the mean field theory. Experimental
measurements for variation of the order parameters
(wavenumber position and width) with temperature, have
been interpreted using Landau–Devonshire thermodynamic
formalism for bulk perovskites in the case of thin films
of BaTiO\(_3\).\(^{13}\) For the C–T phase transition of BaTiO\(_3\), the
quadrupole coupling constant (order parameter) has been
analyzed as a function of temperature using the experimental
measurements for barium titanate nanoparticles on the basis
of the Landau expansion of the free-energy density.\(^{15}\) Very
recently, we have analyzed\(^{22}\) the temperature dependence of the
polarization and the dielectric susceptibility near the C–T
transition by using the experimental data for the lattice mode
(order parameter) of thin films in BaTiO\(_3\) according to the
Landau phenomenological theory.

In this study, by presenting the Landau mean field model
we predict the temperature and pressure dependence of the
spontaneous polarization from that dependence of the di-
electric susceptibility for the ferroelectric–paraelectric (C–T)
transition in BaTiO\(_3\). Experimental data are used to analyze
the critical behavior of the dielectric susceptibility, as
also analyzed previously\(^{3}\) and the critical exponents are de-
cided for the spontaneous polarization in the classical and
quantum limits for the ferroelectric–paraelectric transition in
BaTiO\(_3\).

Below, in Sec. 2, we introduce the Landau mean field model
and give our calculations and results. We discuss our
results in Sec. 3. Conclusions are given in Sec. 4.

## 2. Calculations and Results

We calculate here the spontaneous polarization as functions
of temperature and pressure from the dielectric susceptibility
close to the cubic tetragonal transitions in BaTiO\(_3\) which
exhibits first-order transition. However, above 3 GPa, the
first-order and second-order transitions crossover at the crit-
cal point in BaTiO\(_3\).\(^{2}\) Our analysis of the experimental data
using Landau phenomenological theory is based on both first-
order and second-order transitions which occur in BaTiO\(_3\).

In the Landau phenomenological theory, the free energy
of a ferroelectric material can be expressed in terms of the
spontaneous polarization \( P \) as

\[
F = a_0 + a_2 P^2 + a_4 P^4,
\]

with the \( \alpha \), \( a_0 \) and \( a_4 \) as constants. \( T_C \) is the Curie
temperature.

In the paraelectric phase \((T > T_C)\), we have \( P = 0 \)
whereas in the ferroelectric phase \((T < T_C)\), \( P \neq 0 \).
From the minimization of ferroelectric free energy,
\( \partial F/\partial P = 0 \), we have

\[
2P(a_2 + 2a_4P^2) = 0.
\]

This gives the solutions,

\[
P = 0 \quad \text{(paraelectric phase)}
\]

and

\[
P^2 = -a_2/2a_4 \quad \text{(ferroelectric phase)}.
\]

Also, the temperature dependence of the inverse suscep-
tibility \((\chi^{-1})\) can be derived from Eq. (1) by defining

\[
\chi^{-1} = \frac{\partial^2 F}{\partial P^2}
\]

which gives

\[
\chi^{-1} = 2a_2 + 12a_4P^2.
\]

When \( P = 0 \) in the paraelectric phase \((T > T_C)\), we obtain

\[
\chi^{-1} = 2a_2
\]

so, the temperature dependence of the inverse susceptibility is
given by

\[
\chi^{-1} = 2\alpha(T - T_C).
\]

In the ferroelectric phase \((T < T_C)\) from Eq. (5) by using
Eq. (2), we obtain

\[
\chi^{-1} = 2\alpha(T - T_C) + 12a_4P^2.
\]

Thus, from the mean-field theory, the value of the critical
exponent is deduced as \( \gamma_r = 1 \) for the inverse susceptibility
according to the power law formula in the paraelectric phase,

\[
\chi^{-1} \propto (T - T_C)^{\gamma_r}.
\]

Also, in the ferroelectric phase, this theory predicts that the
critical exponent \( \beta \) for the polarization is \( \beta = 1/2 \) according to

\[
P = c(T - T_C)^{\beta},
\]

where \( c \) is the amplitude.

By analyzing the experimental data for the inverse di-
electric susceptibility, Ishidate et al.\(^{3}\) obtained the values
of \( \gamma_r = 1.2 \) at 4 GPa for the paraelectric phase \((T > T_C)\)
in the classical limit \((T_C = 212K)\) for the C–T transition in BaTiO\(_3\).
Their value was \( \gamma_r = 1.7 \) at 7 GPa for the paraelectric phase
\((T > T_C)\) in the quantum limit \((T_C = 0 \text{K})\). For both analyses,
they used the power law formula,

\[
\chi^{-1} = b(T - T_C)^{\gamma_r}
\]

with the critical exponent \( \gamma_r \) for the dielectric susceptibility \( \chi \)
and the amplitude \( b \).
Using the temperature dependence of the inverse susceptibility $\chi^{-1}$ (Eq. (8)) and the spontaneous polarization $P$ (Eq. (10)) for the ferroelectric phase, we find through Eq. (11),

$$b(T - T_c)^{\gamma - 1} = 2\alpha + 12a_4c^2(T - T_c)^{2\beta - 1}.$$  \hspace{1cm} (12)

This then gives

$$(T - T_c)^{\gamma - 1} \sim (T - T_c)^{2\beta - 1}$$ \hspace{1cm} (13)

with

$$\beta_T = \gamma_T/2.$$ \hspace{1cm} (14)

In the classical limit $\gamma_T = 1$ and $\beta = 1/2$, whereas in the quantum limit $\gamma_T = 2$ and $\beta = 1$ (Eq. (14)). For the paraelectric phase at 4 GPa ($T_c = 212$ K), we then find $\beta = 1.2/2 = 0.6$ since $\gamma_T = 1.2$ and at 7 GPa ($T_c = 212$ K) $\beta = 1.7/2 = 0.85$ with $\gamma_T = 1.7$.3

From the analysis of their experimental results for the inverse dielectric susceptibility, Ishidate et al.3 obtained $\gamma_T$ values at various pressures for BaTiO3, as given in Table 1. In this table, we also give our $\beta$ values according to Eq. (14).

The pressure dependence of the inverse dielectric susceptibility $\chi$ and also the spontaneous polarization $P$ at constant temperature can be obtained close to the transition point in BaTiO3. By considering in the free energy expansion (Eq. (1))

$$a_2 = a_{20}(p - p_c),$$ \hspace{1cm} (15)

where $a_{20}$ is constant and $p_c$ is the critical pressure from Eq. (6) through Eq. (15) in the paraelectric phase ($P = 0$), the pressure dependence of the inverse susceptibility can be written as

$$\chi^{-1} = 2a_{20}(p - p_c).$$ \hspace{1cm} (16)

In the ferroelectric phase, using Eq. (5) the inverse susceptibility can be obtained at various pressures as follows:

$$\chi^{-1} = 2a_{20}(p - p_c) + 12a_4P^2.$$ \hspace{1cm} (17)

Thus, from the mean-field theory, the critical exponent is $\gamma_p = \gamma_T = 1$ for the inverse susceptibility in the classical limit according to the power-law formula

$$\chi^{-1} \propto (p - p_c)^{\gamma_p}$$ \hspace{1cm} (18)

in the paraelectric phase.

3. Discussion

We studied the temperature dependence of the spontaneous polarization and dielectric susceptibility (dielectric constant) close to the ferroelectric–paraelectric transition in BaTiO3 using the mean field theory. Expressions for the spontaneous polarization (ferroelectric phase) and the dielectric susceptibility (ferroelectric and paraelectric phases) were derived. The critical behavior of the dielectric susceptibility and the spontaneous polarization was described by a power-law formula with the critical exponents $\gamma_p$ and $\beta_T$, respectively, close to the ferroelectric–paraelectric transition in BaTiO3. It was found that $\beta_T = \gamma_T/2$, and using the $\gamma_T$ values as obtained from the analysis of Ishidate et al.,3 we extracted the $\beta_T$ values for the spontaneous polarization in the ferroelectric phase of BaTiO3. Those values of the critical exponents were obtained between $\gamma_T = 1$, $\beta_T = 1/2$ (classical limit) and $\gamma_T = 2$, $\beta_T = 1$ (quantum limit) for the ferroelectric–paraelectric transition in BaTiO3. From the analysis of the experimental measurements of the dielectric susceptibility, values of the critical exponent were obtained as $\gamma_T = 1.2$ (at 4 GPa) and $\gamma_T = 1.7$ (at 7 GPa) by Ishidate et al.3 in the classical and quantum limits, respectively, for BaTiO3. This led us to extract the values of $\beta_T = 0.60$ (classical limit) and $\beta_T = 0.85$ (quantum limit) according to Eq. (14) as given in Table 1.

We extended this study to the pressure dependence of the dielectric susceptibility $\chi$ and the spontaneous polarization $P$ at constant temperatures of 100 and 200 K using the experimental data3 for the paraelectric–ferroelectric transition in BaTiO3. Using the mean field theory by expanding the free energy in terms of the order parameter (spontaneous polarization), we obtained the pressure dependencies of both spontaneous polarization $P$ and the dielectric susceptibility $\chi$, as we obtained for the temperature dependence of $P$ and $\chi$. 

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Table 1. Values of the critical exponents $\gamma_T$ and $\beta_T$ for the dielectric susceptibility $\chi$ and the spontaneous polarization $P$, respectively, at various pressures close to the C–T transition in BaTiO3.

| P (GPa) | $\gamma_T$ | $\beta_T$ |
|--------|------------|-----------|
| 2.99   | 0.99       | 0.50      |
| 3.99   | 1.20       | 0.60      |
| 4.98   | 1.70       | 0.85      |
| 5.97   | 1.49       | 0.75      |
| 6.98   | 1.70       | 0.85      |
| 7.97   | 1.20       | 0.60      |
From the pressure dependence of the dielectric susceptibility $\chi$ (Eq. (20)), Ishidate et al. concluded that the critical exponent value of $\gamma_p = 1$ as predicted from the quantum theory, is valid at constant temperatures of 100 and 200 K in the cubic (paraelectric) phase of BaTiO$_3$. This implies from the pressure dependence of the spontaneous polarization $P$ (Eq. (19)), the critical index $\beta_p = 1/2$ (Eq. (23)) is also valid in the quantum limit. This is due to the fact that in the quantum limit, the critical temperature $T_c$ depends on the interaction parameter $S$ (an external parameter such as pressure or chemical composition) according to

$$T_c(S) \propto (S_c - S)^{1/\phi},$$  \hspace{1cm} (24)

where the critical exponent $\phi$ is equal to 2 (in the classical limit $\phi = 1$). In Eq. (24), $S_c$ is the value of the interaction parameter at $T_c = 0$. Thus, from Eqs. (9) and (24) through Eq. (20), one finds

$$\gamma_p = \gamma_T/\phi$$  \hspace{1cm} (25)

which is equal to 1 at $T_c = 0$ according to the quantum theory.

This gives $\gamma_T = 2$ in the quantum limit and $\gamma_T = 1$ in the classical limit, as stated above. Therefore, we conclude on the basis of the $\gamma_p = 1$ value that our value of $\beta_p = 1/2$ for the spontaneous polarization is valid in the quantum limit ($T_c = 0$) and also at constant temperatures of 100 and 200 K in the cubic phase of BaTiO$_3$.

4. Conclusions

Critical behavior of the dielectric susceptibility and the spontaneous polarization was analyzed for the ferroelectric-paraelectric phase transition in BaTiO$_3$. This analysis was employed on the basis of the Landau mean field theory and from the values of the critical exponent $\gamma$ for the dielectric susceptibility, the $\beta$ values for the spontaneous polarization were extracted according to $\beta = \gamma/2$ between the classical and quantum limits for the ferroelectric-paraelectric transition in BaTiO$_3$.

Similar method of analysis can be done for some other ferroelectric materials which undergo successive phase transitions such as BaTiO$_3$.

References

1. F. Jona and G. Shirane, Ferroelectric Crystals, Chapters 4 and 5 (The Macmillan Company, New York, 1962).
2. G. A. Samara, Pressure and temperature dependences of the dielectric properties of the perovskites BaTiO$_3$ and SrTiO$_3$, Phys. Rev. 151, 378 (1966).
3. T. Ishidate, S. Abe, H. Takahashi and N. Mori, Phase diagram of BaTiO$_3$, Phys. Rev. Lett. 78, 2397 (1997).
4. Y. Akishige, H. Takahashi, N. Mori and E. Sawaguchi, Vanishing of the phase transitions in ferroelectric hexagonal BaTiO$_3$ at high pressure, J. Phys. Soc. Jpn. 63, 1590 (1994).
5. Y. Akishige, T. Atake, Y. Saitoh and E. Sawaguchi, Specific heat of hexagonal barium titanate, J. Phys. Soc. Jpn. 57, 718 (1988).
6. D. Heiman and S. Ushioda, Dispersion of the soft E-mode polarization in BaTiO$_3$, Phys. Rev. 9, 2122 (1974).
7. Y. Tomihaga and T. Nakamura, Temperature dependence of dispersion relation of over-damped E-polarisation in BaTiO$_3$, J. Phys. Soc. Jpn. 39, 746 (1975).
8. A. Scalabria, A. S. Chaves, D. S. Shim and S. P. S. Porto, Temperature dependence of the $A_1$ and $E$ optical phonons in BaTiO$_3$, Phys. Stat. Sol. B 79, 731 (1977).
9. L. Verble, E. Gallego-Lluesma and S. P. S. Porto, First-order $A_1$ (TO) phonons as evidence of disorder in BaTiO$_3$, J. Raman Spectrosc. 7, 7 (1978).
10. Y. Laspin, J. L. Servoin and F. Gervais, Soft mode spectroscopy in barium titanate, J. Phys. C: Solid State Phys. 13, 3761 (1980).
11. K. Inoue, A. Hasegawa, K. Watanabe, H. Yamaguchi, H. Uwe and T. Sakudo, Silent soft mode in hexagonal barium titanate observed by hyper-Raman scattering, Phys. Rev. B 38, 6352 (1988).
12. M. Yamaguchi, M. Watanabe, K. Inoue, Y. Akishige and T. Yagi, Light scattering study of the coupled soft-optic and acoustic mode in hexagonal barium titanate, Phys. Rev. Lett. 75, 1399 (1995).
13. S. Gupta, Investigations of micro-stress and phase transition in sol-gel-derived multideposited coatings of barium titanate using Raman spectroscopy, J. Raman Spectrosc. 33, 42 (2002).
14. M. El Marssi, F. Le Marrec, I. A. Lukyanchuk and M. G. Karkut, Ferroelectric phase in barium titanate epitaxial thin film, Ferroelectrics 291, 55 (2003).
15. P. Sedykh and D. Michel, Ferroelectric phase transition in barium titanate nanoparticles, Phys. Rev. B 79, 134119 (2009).
16. A. Kiraci and H. Yurtseven, Temperature dependence of the Raman frequency, damping constant and the activation energy of a soft-optic mode in ferroelectric barium titanate, Ferroelectrics 432, 14 (2012).
17. H. Yurtseven and A. Kiraci, Calculation of the damping constant and the relaxation time for the soft-optic and acoustic mode in hexagonal barium titanate, Ferroelectrics 437, 137 (2012).
18. A. Kiraci and H. Yurtseven, Damping constant calculated as a function of temperature for the tetragonal Raman mode close to the paraelectric-ferroelectric transition in BaTiO$_3$, Ferroelectrics 450, 93 (2013).
19. W. Heywang, J. Am. Cer. Soc. 47, 484 (1964).
20. K. H. Cho and H. Y. Lee, Pore dependent dielectric and electrical properties of barium titanate ceramic, Proc. IEEE (1995) 566.
21. S. Yasmin, S. Choudhury, M. A. Hakim, A. H. Bhuiyan and M. J. Rahman, structural and dielectric properties of pure and cerium doped barium titanate, J. Cer. Proc. Res. 12, 387.
22. H. Yurtseven and A. Kiraci, Temperature dependence of the polarization and dielectric constant near the paraelectric-ferroelectric transition in BaTiO$_3$, J. Mol. Model. 19, 3925 (2013).
23. T. Schneider, H. Beck and E. Stoll, Phys. Rev. B 13, 1123 (1976).
24. R. Morf, T. Schneider and E. Stoll, Phys. Rev. B 16, 462 (1977).