ORIGINAL PAPER

Temperature dependence of the polarization and the dielectric constant near the paraelectric-ferroelectric transitions in BaTiO$_3$

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Abstract Temperature dependences of the spontaneous polarization and the dielectric constant are calculated near the paraelectric-ferroelectric (cubic-tetragonal) transition in BaTiO$_3$ using our mean field model. By expanding the free energy in terms of the spontaneous polarization (order parameter), expressions for the temperature dependence of the spontaneous polarization and the dielectric constant are derived. By considering the temperature dependence of the Raman frequencies for the lattice mode (~310 cm^{-1}) which is related to the spontaneous polarization, the experimental data from the literature is analyzed near the first order paraelectric-ferroelectric transition in BaTiO$_3$. The dielectric constant is then calculated as a function of temperature for the cubic-tetragonal transition in BaTiO$_3$. Our results show that the observed behavior of the spontaneous polarization in the ferroelectric phase ($T<T_C$) and that of the dielectric constant in both paraelectric ($T>T_C$) and ferroelectric phases, can be described adequately by the mean field model studied here for BaTiO$_3$.

Keywords BaTiO$_3$ · Dielectric constant · Paraelectric-ferroelectric transition · Spontaneous polarization

Introduction

BaTiO$_3$ exhibits the ferroelectric-paraelectric transition at the Curie temperature. Above 120 °C the dielectric constant ε obeys the Curie-Weiss law and shortly before the ε diverges at the Curie point, a permanant polarization P develops in the BaTiO$_3$ crystallites [1]. Curie-Weiss behavior of the dielectric constant in the cubic paraelectric phase was studied many

years ago and this behavior was attributed to anharmonic contributions to the potential energy [2]. The temperature (to 150 °C) and pressure (to 25 kbar) dependences of the polarization P and the dielectric constant ε were also studied, and the T-P phase diagram was obtained experimentally [3, 4]. Phase diagram of BaTiO$_3$ has been calculated using density functional form [5].

From the infrared reflectivity measurements [6] in the cubic paraelectric phase of BaTiO$_3$ (T$_C$=395 K) for the temperature dependences of TO and LO frequencies, damping and TO oscillator strengths, it was indicated that an overdamped soft mode deviates from the Curie-Weiss law over hundred degrees above the tetragonal-cubic transition. More recently, pore-dependent dielectric and electrical properties of barium titanate ceramic has been studied and the abrupt decrease of both dielectric constant and Curie temperature was obtained as porocity increased [7].

Raman investigations of the tetragonal (ferroelectric) phase have been reported in the literature [6, 8–12]. From the low-frequency light scattering spectra of hexagonal barium titanate (h-BaTiO$_3$) which exhibits successive structural phase transitions at T$_0$=222 K (ferroelectric) and T$_C$=74 K (ferroelastic), a coupled soft-optic and acoustic mode model has been employed [10]. Very recently, we have also studied soft-optic mode in ferroelectric barium titanate [13] and, the soft-optic and acoustic mode in hexagonal barium titanate [14]. From the ^{137}Ba NMR measurements on BaTiO$_3$ powders, the cubic-tetragonal phase transition has been studied using the Landau phenomenological theory [15].

In this study, we also use the Landau phenomenological theory to calculate the temperature dependence of the spontaneous polarization P and of the dielectric susceptibility χ (dielectric constant ε) for the tetragonal-cubic phase transition in BaTiO$_3$. By expanding the free energy in terms of the order parameter (spontaneous polarization), expressions for the temperature dependence of P and χ are derived. Our expression for the spontaneous polarization P is fitted to

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the experimental data [16] for the temperature dependence of the wavenumber position of the Raman mode (310 cm^{-1}) for thin films (60 nm and 200 nm) in BaTiO$_3$. By determining the fitting parameters, the temperature dependence of the inverse dielectric susceptibility in the ferroelectric and paraelectric phases for both thin films in BaTiO$_3$ is calculated.

Below, in "Theory" we give an outline of our mean field model. In "Calculations and results", our calculations and results are shown. Discussion of our results and conclusions are given in "Discussion" and "Conclusions", respectively.

Theory

The free energy can be expanded in terms of the spontaneous polarization P for the paraelectric-ferroelectric phase transition in BaTiO$_3$, as follows:

$$F = a_0 + a_2 P^2 + a_4 P^4 + a_6 P^6 \qquad (1)$$

In Eq. (1) the coefficient a_2 can be taken to be the temperature dependent,

$$a_2 = a(T - Tc), \qquad (2)$$

where a is a positive constant, and all the other coefficients (a_0, a_4 and a_6) are assumed to be constant.

The temperature dependence of the spontaneous polarization P and the dielectric susceptibility χ (or dielectric constant, $\varepsilon = \chi + 1$) can be derived from the free energy (Eq. 1). From the minimization of the free energy $\partial F / \partial P = 0$, one gets

$$a_2 + 2a_4 P^2 + 3a_6 P^4 = 0, \qquad (3)$$

which can be solved for the spontaneous polarization P as

$$P^2 = \frac{a_4}{3a_6} \pm \frac{1}{3a_6} \sqrt{a_4^2 - 3a_2 a_6} \qquad (4)$$

By taking $a_4 < 0$ and $a_6 > 0$, a positive P solution of Eq. (4) defines the ferroelectric phase ($T < T_C$) whereas $P = 0$ corresponds to the paraelectric phase for $T > T_C$ in BaTiO$_3$. Using Eq. (2), the temperature dependence of the spontaneous polarization P can be obtained from Eq. (4).

Similarly, the temperature dependence of the dielectric susceptibility χ can be obtained according to the definition

$$\chi^{-1} = \left(\partial^2 F / \partial P^2 \right), \qquad (5)$$

which gives

$$\chi^{-1} = 2a_2 + 12a_4 P^2 + 30a_6 P^4 \qquad (6)$$

In the paraelectric phase ($P = 0$), the reciprocal dielectric susceptibility χ^{-1} or the dielectric constant ε becomes

$$\chi^{-1} = (\varepsilon - 1)^{-1} = 2a_2 \qquad (7)$$

In the ferroelectric phase ($P \neq 0$) using Eq. (4) in Eq. (6), χ^{-1} can be expressed in terms of the coefficients a_2, a_4 and a_6. By Eq. (2), the temperature dependence of χ^{-1} can be obtained. Since the functional form of P^2 (Eq. (4)) is rather long, the temperature dependence of the spontaneous polarization P and the dielectric susceptibility χ can be obtained approximately by making an ansatz,

$$\frac{a_2 a_6}{a_4^2} \langle\langle 1, \qquad (8)$$

which gives the root square in the P^2 expression (Eq. 4) as

$$\left(a_4^2 - 3a_2 a_6 \right)^{1/2} = a_4 - \frac{3}{2} \frac{a_2 a_6}{a_4} \qquad (9)$$

By considering the minus solution in the root square of Eq. (4), the spontaneous polarization P can be obtained as

$$P^2 = -\frac{2a_4}{3a_6} + \frac{a_2}{2a_4} \qquad (10)$$

With this ansatz, we get the spontaneous polarization in the simplified form (Eq. 10) in comparision with Eq. (4).

Similarly, using Eq. (10) in Eq. (6) through the ansatz (Eq. 8) the expression for χ^{-1} can be written in the simplified form as

$$\chi^{-1} = (\varepsilon - 1)^{-1} = -12a_2 + \frac{16}{3} \frac{a_4^2}{a_6} \qquad (11)$$

in the ferroelectric phase. Using the simplified forms of the spontaneous polarization P (Eq. 10) and the reciprocal dielectric susceptibility χ^{-1} (Eq. 11), their temperature dependence in the ferroelectric phase can then be obtained according to Eq. (2), which gives

$$P^2 = \frac{\alpha(T - T_C)}{2a_4} - \frac{2a_4}{3a_6} \qquad (12)$$

$$\chi^{-1} = -12\alpha(T - T_C) + \frac{16}{3} \frac{a_4^2}{a_6} \qquad (13)$$

In the paraelectric phase ($P = 0$), the temperature dependence of the reciprocal dielectric susceptibility χ^{-1} will be obtained as

$$\chi^{-1} = 2\alpha(T - T_C) \qquad (14)$$

according to Eq. (7) through Eq. (2).

Calculations and results

The temperature dependence of the spontaneous polarization P was calculated using the experimental data [16] for the peak positions (frequency) of the lattice phonon ($\sim$310 cm^{-1}) from the Raman spectroscopic measurements in the ferroelectric phase of BaTiO$_3$. This was performed by the temperature dependence of the Raman frequency near the paraelectric-ferroelectric transition according to a power-law formula

$$\omega^2 \alpha (T - T_C). \tag{15}$$

Since the peak position of the 310 cm^{-1} mode decreased considerably as the transition temperature T_C was approached from the ferroelectric phase, as observed experimentally [16], this phonon frequency was associated with the order parameter (spontaneous polarization) in this crystal. Thus, in our analysis the temperature dependence of the Raman peak position of the 310 cm^{-1} mode (Eq.15) was correlated to the spontaneous polarization P (Eq. 12) which gives

$$\left(\omega / \omega_{max}\right)^2 = \frac{\alpha(T - T_C)}{2a_4} - \frac{2a_4}{3a_6}. \tag{16}$$

Since the order parameter (spontaneous polarization P) varies from 0 to 1, we normalized the Raman frequency ω of this phonon with respect to its maximum value ω_{max}.

We analyzed the temperature dependence of the observed [16] Raman frequencies for the 310 cm^{-1} mode for thin films of 60 and 200 nm in BaTiO$_3$. By fitting Eq. (16) to the observed Raman frequency data [16], the fitted parameters were determined, as given in Table 1. For this determination of α and a_4, we took $a_6 = 1$ regarding both thin films (Table 1). We plot square of the frequency ratio ω/ωmax as a function of temperature close to the ferroelectric-paraelectric transition in BaTiO$_3$ for thin films (60 nm in Fig. 1 and 200 nm in Fig. 2).

Using the fitting parameters α and a_4 ($a_6 = 1$), we calculated the temperature dependence of the inverse susceptibility χ^{-1} in the ferroelectric phase according to Eq. (13). We also calculated the temperature dependence of χ^{-1} for the paraelectric phase using Eq. (14) for both thin films (60 and 200 nm), as plotted in Figs. 3 and 4, respectively.

Table 1 Values of the temperature T$_C$, the parameters α and a_4 (Eq. 12) for the ferroelectric-paraelectric transition for the thin films indicated in BaTiO$_3$

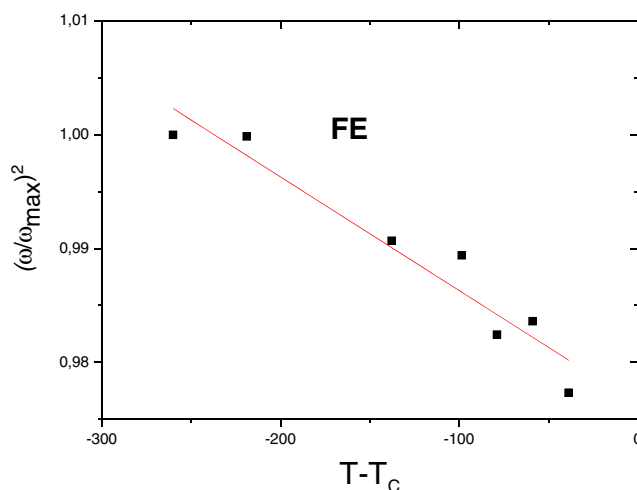| Thin films (nm)	T_C(K)	α (10^{-5} 1/K)	a_4
60	360	9.759	−0.488
200	440	9.490	−0.484

Fig. 1 Temperature dependence of the square of the frequency ratio ω/ω_{max} of the 310 cm^{-1} Raman mode (correlated to the spontaneous polarization P) for the ferroelectric (FE)—paraelectric (PE) transition using the thin film of 60 nm according to Eq. (16) in BaTiO$_3$. The observed data [16] is also shown here

Discussion

The Raman frequency of the lattice phonon ($\sim$310 cm^{-1}) which is associated with the order parameter (spontaneous polarization) was analyzed at various temperatures according to Eq. (16) or Eq. (12) using the experimental data [16], as plotted in Figs. 1 and 2. This analysis was carried out for thin films of 60 nm (Fig. 1) and 200 nm (Fig. 2), as stated above. It was found that the temperature dependence of ω^2 or P^2 is linear for both films in the ferroelectric phase of BaTiO$_3$. This is in accordance with the mean field theory where $P \propto (T - T_C)^\beta$ with $\beta = 1/2$ as the critical exponent for the order parameter. Our calculated values for the $(\omega/\omega_{max})^2$ as a function of the reduced temperature (T−T$_C$) can
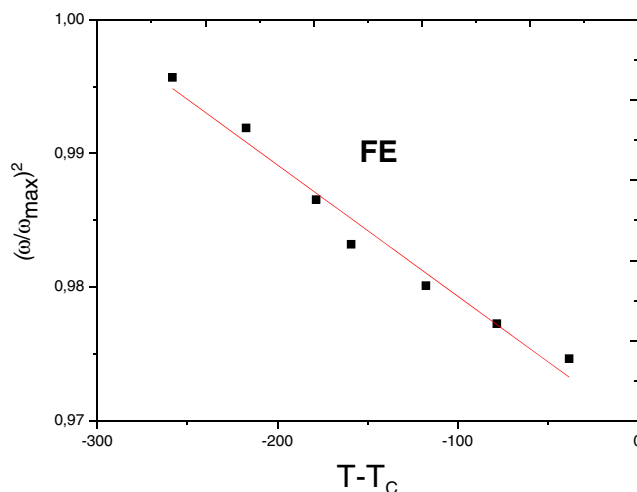

Fig. 2 Temperature dependence of the square of the frequency ratio ω/ω_{max} of the 310 cm^{-1} Raman mode (correlated to the spontaneous polarization P) for the ferroelectric (FE)—paraelectric (PE) transition using the thin film of 200 nm according to Eq. (16) in BaTiO$_3$. The observed data [16] is also shown here
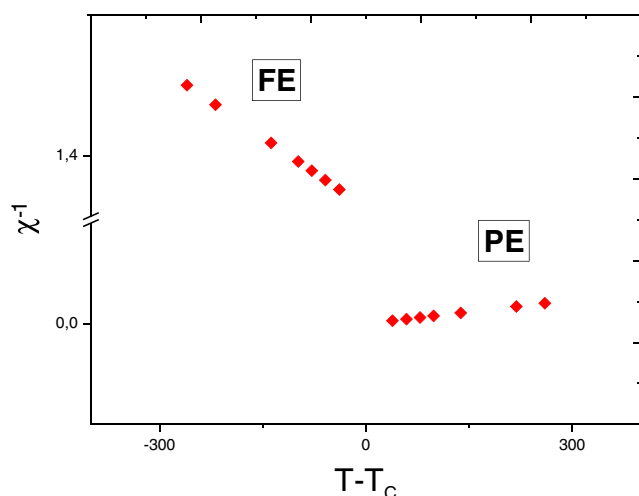
Fig. 3 Temperature dependence of the inverse dielectric susceptibility χ^{-1} (dielectric constant ε) for the ferroelectric (FE)—paraelectric (PE) transition using the thin film of 60 nm according to Eq. (13) (FE) and Eq. (14) (PE) in BaTiO$_3$

Fig. 5 The observed spontaneous polarization P_S^2 of single-crystal BaTiO$_3$ as a function of the reduced temperature (T−T$_C$) [3]. P_S^2 was normalized with respect to its maximum value

be compared with the experimental data for the spontaneous polarization P_S in the ferroelectric phase (FE) for thin films of 60 and 200 nm in BaTiO$_3$. Unfortunately, we have been unable to compare our calculated values of $(\omega/\omega_{max})^2$ with the observed P_S^2 data since there is no experimental data available in the literature for thin films of 60 and 200 nm in BaTiO$_3$. In order to see the behavior of $(\omega/\omega_{max})^2$ as a function of the reduced temperature of T−T$_C$ in the ferroelectric phase (FE) for thin films of 60 and 200 nm (Figs. 1 and 2), we compared our calculated values of $(\omega/\omega_{max})^2$ with the temperature dependence of the observed [3] spontaneous polarization (P_S^2) of single-crystal BaTiO$_3$, as plotted in Fig. 5. This experimental data [3] was obtained for the reduced temperature range of −80 K< T − T$_C$ <0 K for constant pressures of 1, 4, 8 and 12 kbar in this crystal. When plotted the spontaneous polarization P_S as a function of

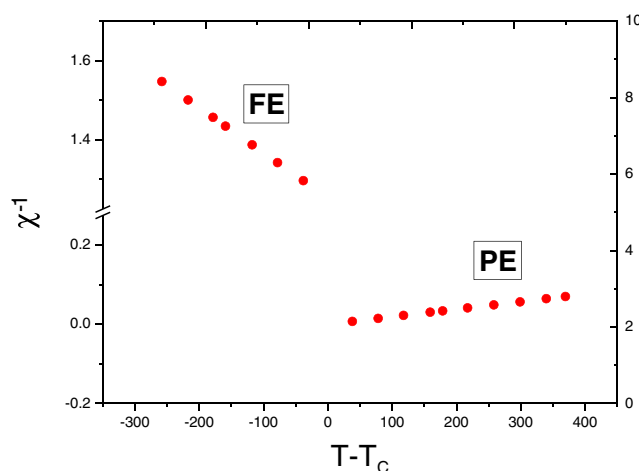the reduced temperature T−T$_C$, all the experimental data points are almost at the same positions which decreases continuously as T−T$_C$ decreases. This then gives rise to a linear variation of P_S^2 with the T−T$_C$, as plotted in Fig. 5. Thus, a linear variation of the observed spontaneous polarization P_S^2 [3] with the reduced temperature T−T$_C$ within the temperature range of −80 K< T − T$_C$<−20 K (Fig. 5) is the same as the calculated $(\omega/\omega_{max})^2$ for thin films of 60 and 200 nm within the temperature range of −250 K< T − T$_C$ < −50 K in the ferroelectric (FE) phase of BaTiO$_3$.

In regard to the inverse susceptibility χ^{-1} or the dielectric constant ($\varepsilon = \chi + 1$), which was calculated using the parameters of the spontaneous polarization (Eq. 12) also shows a linear variation with the temperature, as plotted in Figs. 3 and 4 according to Eqs. (13) and (14) in the ferroelectric and paraelectric phases, respectively, for both thin films (60 and 200 nm) in BaTiO$_3$. This is also expected from the mean field theory according to a power-

Fig. 4 Temperature dependence of the inverse dielectric susceptibility χ^{-1} (dielectric constant ε) for the ferroelectric (FE)—paraelectric (PE) transition using the thin film of 200 nm according to Eq. (13) (FE) and Eq. (14) (PE) in BaTiO$_3$
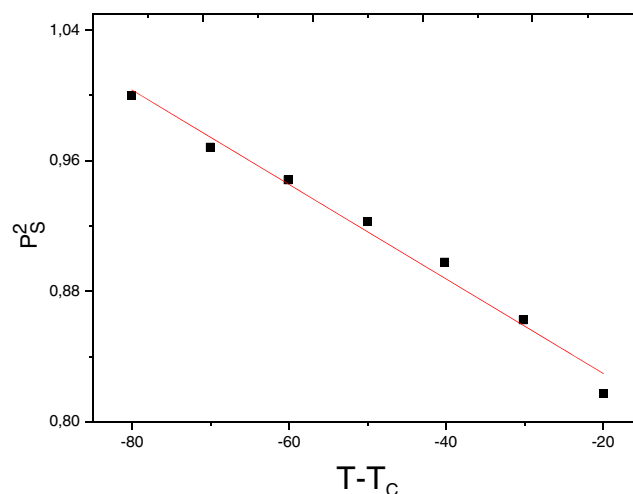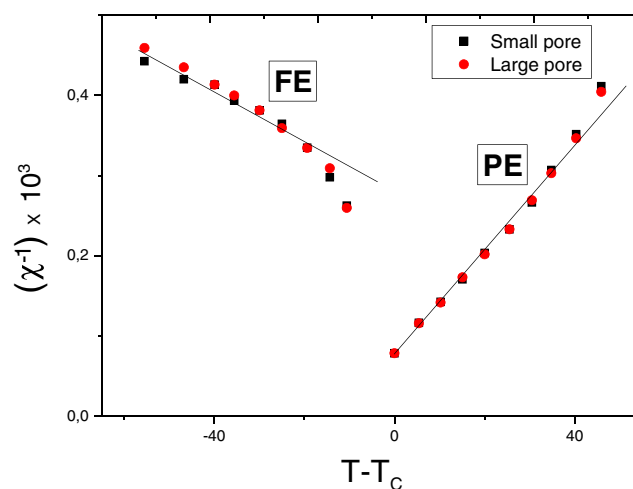

Fig. 6 Inverse susceptibility (χ^{-1}) obtained from the observed dielectric constant (ε) [7] as a function of the reduced temperature for barium titanate ceramics with different porosities and pore size (5 %)
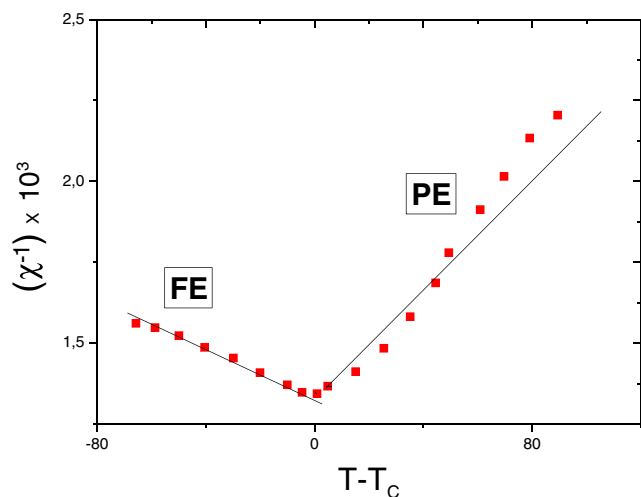
Fig. 7 Variation of the inverse susceptibility (χ^{-1}) obtained from the experimental dielectric constant (ε) [27] with the reduced temperature at three frequencies (10, 100 and 1000 kHz) of $Ba_{1-x}Ce_xTiO_3$ for x=0 ($BaTiO_3$)

law formula $\chi \propto (T-T_C)^{-\gamma}$ with the $\gamma=1$ value for both phases above and below T_C. As for our values of $(\omega/\omega_{max})^2$, the calculated values of the inverse susceptibility (χ^{-1}) as a function of the reduced temperature ($T-T_C$) as plotted in Figs. 3 and 4, can also be compared with the observed χ^{-1} or the dielectric constant ε in the ferroelectric (FE) and paraelectric (PE) phases of $BaTiO_3$. Since there is no experimental data in the literature for the dielectric constant for thin films of 60 and 200 nm in $BaTiO_3$, the closest experimental data available was the dielectric constant at various temperatures near the ferroelectric-paraelectric transition for barium titanate ceramics with different porosities and pore sizes [7]. In the case of small and large pores (5 %) for the observed dielectric constant ε, we plot the inverse susceptibility χ^{-1} against $T-T_C$ in Fig. 6 for the ferroelectric (FE) and paraelectric (PE) phases in $BaTiO_3$ ceramics which can be compared with our calculated values of χ^{-1} in Figs. 3 and 4 for thin films of 60 and 200 nm in this crystal. For those plots (Figs. 3, 4 and 6), we see that the inverse susceptibility (χ^{-1}) decreases as the T_C is approached in both ferroelectric (FE) and paraelectric (PE) phases in this crystalline system. Also, for comparision purposes, we analyzed recent experimental data [27] for the dielectric constant (ε) as a function of temperature at three frequencies (10, 100 and 1000 kHz) of $Ba_{1-x}Ce_xTiO_3$ compounds for x=0 ($BaTiO_3$). We plot the inverse susceptibility(χ^{-1}) against $T-T_C$ in both ferroelectric (FE) and paraelectric (PE) phases, as shown in Fig. 7. We also see similar behavior of χ^{-1} as our calculated χ^{-1} (Figs. 3 and 4) and also the observed χ^{-1} (Fig. 6). As given in our calculated values of χ^{-1} (Figs. 3 and 4), the reduced temperature (-300 K< $T - T_C$ < 300 K) is much wider than the experimentally obtained temperature range (-40 K< $T-T_C$ <40 K in Fig. 6) and (-80 K< $T-T_C$ < 80 K in Fig. 7). Our results show that the temperature dependent

behavior of the $BaTiO_3$ film is qualitatively similar to that observed for single crystal $BaTiO_3$ and barium titanate ceramic.

The spontaneous polarization P was calculated by analyzing the temperature dependence of the Raman frequency of the 310 cm^{-1} lattice mode according to Eq. (15) in the ferroelectric phase of $BaTiO_3$. This temperature dependence of the frequency was also studied previously for the translational optic (TO) mode in the cubic paraelectric phase of $BaTiO_3$ [4]. The soft mode damping was studied experimentally [6] and was discussed in the framework of the soft-mode theory of Landau and Cochran. By relating the temperature dependence of a bilinear coupling constant A between acoustic and soft-optic modes to the order parameter Q_3 according to the power-law formula

$$A \sim (T-T_0)^{1/2} \qquad (17)$$

the hexagonal- $BaTiO_3$ was studied above the transition temperature ($T_0=222$ K) in the paraelectric phase [10]. Equation (17) was also used to analyze the experimental data [10] to calculate the damping constant and the relaxation time for the soft-optic and acoustic mode in hexagonal-$BaTiO_3$ in our recent study [14].

For the tetragonal phase of $BaTiO_3$, the quadrupole coupling constant C_Q which can be measured in this phase, has been related to the spontaneous ferroelectric polarization for a first order transition according to a power-law expression

$$C_Q \propto (T_f-T)^{\beta}, \qquad (18)$$

where T_f is the upper stability limit ($T_f=403.5$ K) of the ferroelectric phase and it was found that the β value was less than 1/2 [15]. Since the quadrupole coupling constant C_Q describes the square of the frequency (ω^2) for the Raman mode (310 cm^{-1}), the frequency squared is directly proportional to the square of the order parameter (spontaneous polarization). So, the variation of the Raman frequency and width of this mode with the temperature can be considered as the order parameter (spontaneous polarization) in the ferroelectric (FE) phase of $BaTiO_3$ and the polarization is along the c-axis, as also studied previously [16]. We have related ω/ω_0 (ω_0 is the maximum frequency) of the soft mode to the order parameter S in the ferroelectric phase of KDP (KH_2PO_4) in our previous study [25]. A linear relationship between $(\omega/\omega_{max})^2$ of the internal ammonium mode (ν_3) and P_S^2 (spontaneous polarization) has also been obtained in the ferroelectric phase of$(NH_4)_2SO_4$, as reported in our earlier study [26]. For $BaTiO_3$, we have assumed the same temperature dependence of the soft mode frequency as given by the mean field theory (Eq. 20) and the order parameter P (spontaneous polarization)[14], and a linear variation of ω/ω_0 was obtained with the P in the ferroelectric phase [13]. As observed experimentally [3], before the dielectric constant ε attains its maximum value at the Curie point, a permanent polarization P develops in the $BaTiO_3$

crystallites ($T_C = 110\,°C$) [1]. On the other hand, it was suggested that for the hexagonal $BaTiO_3$ below T_0 (=220 K) the temperature dependence of the Raman frequency of the soft mode can be expressed as

$$\omega_0^2 \propto (T-T_0)^{2/3} \qquad (19)$$

down to 100 K [10]. On the basis of the hard-soft mode coupling model [17–20], the frequency of a coupled mode ω_{sh} can be written [20] as

$$\omega_{sh} \propto (T_C-T)^{1/2}, \qquad (20)$$

similar to Eq. (15) or in general,

$$\omega_{sh} \propto (T_C-T)^{\beta} \qquad (21)$$

as applied to several ferroelectric crystals such as triglycine sulfate (TGS) [21, 22], triammonium hydrogen disulfate, $(NH_4)_3H\ (SO_4)_2$ [23] and lithium ammonium sulfate, $LiNH_4SO_4$ [24]. In those studies, the experimentally measured Raman frequencies were analyzed according to Eq. (21). We have also used hard-soft mode coupling model for various ferroelectric materials such as $BaTiO_3$, KH_2PO_4 (KDP) and $(NH_4)_2SO_4$ in our recent studies [13, 14, 25, 26].

Regarding the temperature dependence of the transverse optic (TO) mode of long wavelength at $k=0$, it was pointed out some years ago [3] that this mode was associated with the reciprocal dielectric constant ε according to

$$\omega_T^2 \propto (T-T_0) \propto 1/\varepsilon, \qquad (22)$$

which is the Curie-Weiss behavior of ε in the cubic phase of $BaTiO_3$. It was indicated that at the critical temperature T_0, $\omega_T \to 0$ and that the lattice displacements associated with this mode become unstable, which causes the crystal to undergo the ferroelectric phase [3]. This dielectric constant ε was measured along the c axis of the $BaTiO_3$ single crystal [3]. In the tetragonal phase anisotropic dielectric constant occurs along the a-axis and c-axis in $BaTiO_3$. In regard to the epitaxial films which are weakly tetragonal, domains are a-axis oriented [12]. When those films are grown at low oxygen pressures, they are tetragonal with the c-axis perpendicular to the plane of the film (c-axis orientation). When they are grown at high oxygen pressure, the epitaxial films are tetragonal with the c-axis in the plane of the film (a-axis orientation), [12]. Although anisotropic dielectric constant occurs in the tetragonal phase along a-axis and c-axis, the tetragonal distortion of the single crystal is nearly equal to unity (c/a≈1.01, $a=3.992\ A^0$ and $c=4.036\ A^0$) [12].

Conclusions

Raman frequencies of the tetragonal 310 cm^{-1} mode were analyzed at various temperatures for ferroelectric-paraelectric transition in $BaTiO_3$. This temperature dependence of the Raman frequency was related to the spontaneous polarization in the tetragonal (ferroelectric) phase of $BaTiO_3$. Using our mean field model, the temperature dependence of the dielectric susceptibility (dielectric constant) was calculated from the spontaneous polarization. It was found that the lattice mode studied here is associated with the ferroelectric-paraelectric phase transition in $BaTiO_3$.

Our predictions for the spontaneous polarization and the dielectric constant at various temperatures can be examined using the experimental data for thin films studied when they are available in the literature.

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