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dc electric-field dependence of the dielectric constant in polar dielectrics: Multipolarization mechanism model

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The dc electric-field dependence of the relative dielectric constant $\varepsilon_r(E)$ in polar dielectrics is studied. The Landau-Ginzburg-Devonshire (LGD) theory and its approximate treatments in dealing with $\varepsilon_r(E)$ are reviewed. It is found that the LGD theory works well in the case of a single polarization mechanism existing in the dielectrics, and the Johnson relation $\varepsilon_r(E)=\varepsilon_r(0)/\{1+\lambda[\varepsilon_0\varepsilon_r(0)]^3E^2\}^{1/3}$ is a reasonable approximate expression describing $\varepsilon_r(E)$. Many polar dielectrics, however, exhibit more than one polarization mechanism contributing to the total dielectric constant. The dielectric response of such polar dielectrics under an external dc electric field cannot be purely described by LGD theory. In this work, we introduce a "reorientational polarization" to describe the "extrinsic" contribution to the dielectric constant, such as might arise from polar clusters, domain-wall motions, fluctuation of microcluster boundaries, defects, etc. A "*multipolarization-mechanism*" model is proposed, and a combined equation $\varepsilon_r(E)=\varepsilon_r(0)/\{1+\lambda[\varepsilon_0\varepsilon_r(0)]^3E^2\}^{1/3}+\Sigma(P_0x/\varepsilon_0)[\cosh(Ex)]^{-2}$ is adopted to describe the total $\varepsilon_r(E)$ response of a polar dielectric, where the first term is Johnson's relation which represents the "intrinsic" polarization, and the latter represents the "extrinsic" polarization. Agreement between the fitting of this equation to the experimental data is obtained for paraelectrics $KTaO_3$ and $Bi:SrTiO_3$.

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I. INTRODUCTION

Dielectric response in polar dielectrics with respect to external temperature, frequency, electric field, and pressure is an important issue in dielectric/ferroelectric physics. In the literature, the dielectric spectra as a function of frequency or temperature have been extensively studied both experimentally and theoretically. For instance, analysis of dielectric relaxation is available via the Debye model (including Cole-Cole equations and related treatments), and the dielectric relaxation rate can be described by the Arrhenius relation, the Vogel-Fulcher relation, or a complicated relaxation-time distribution function.[1–6] However, the dielectric response as a function of electric field, especially up to high field levels, has been studied less due to such difficulties as (i) the difficulty of dielectric measurements under a wide electric field range, especially up to high electric fields, and (ii) lack of a convenient theory (for instance, a simple explicit function) to deal with dielectric spectra as a function of electric field in a wide range.

In fact, the electric-field dependence of the dielectric response can provide very useful information on the basic physics of dielectric polarization. In some cases, such information is critical in understanding the dielectric/ferroelectric behavior in polar dielectrics. In addition, a new type of electronic device making use of the variation of the dielectric constant of polar dielectrics under dc electric fields has been developed recently for allocations in next-generation radar and microwave communication systems.[7–9] Therefore, a study of the dielectric nonlinear behavior under electric fields is also technologically important.

In this paper, we first review the Landau-Ginzburg-Devonshire (LGD) theory and the existing approximate treatments on the electric-field dependence of the dielectric response. It is found that these treatments are insufficient in describing the observed experimental data, which include more than one polarization mechanism. A "multipolarization-mechanism" model is suggested by taking into consideration both the "intrinsic" lattice polarization and the "extrinsic" polarization. These equations are tested by experimental data obtained from $KTaO_3$ and Bi-doped $SrTiO_3$ and good agreement between theory and experimental data is achieved.

II. EXPERIMENTAL PROCEDURE AND RESULTS

In order to test the validity of the theoretical treatments, the dc electric-field dependence of the dielectric constant for (i) *paraelectric* $KTaO_3$ and (ii) dielectric relaxor $Bi:SrTiO_3$ (Ref. 6) was measured using an HP4284A and a Solartron 1260 with an ac field of 2 V/mm under various dc biases at a fixed temperature, at which the sample was allowed to reach thermal equilibration for 15–30 min before the measurement.

The electric-field dependence of the relative dielectric constant (ε_r) for paraelectric $KTaO_3$ in the dc field range ±60 kV/cm is shown in Fig. 1. The dielectric constant is very sensitive to its field history. At 14 K, the dielectric constant at zero field $\varepsilon_r(0)$ is ~2800 for the first run [labeled 1 in Fig. 1(a)], much higher than that of the second and the following runs. The dielectric constant as a function of electric field at 60 K is shown in Fig. 1(b). At 60 K, $\varepsilon_r(0)$ is lower than that at 14 K, and less dependence on the electric-field history is observed at 60 K than at 14 K.

Figure 2 shows the dc electric-field dependence of the dielectric constant (ε_r) for $Bi:SrTiO_3$ with Bi content of 0.2% being recognized as a dielectric relaxor.[6] The dielectric constant is decreased at 13 K with increasing dc field and is

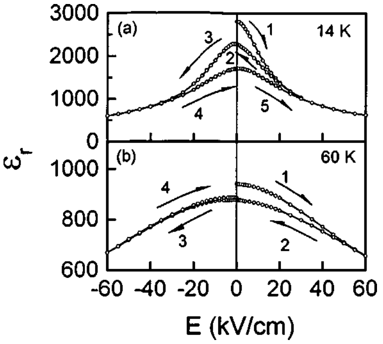

FIG. 1. dc electric-field dependence of the relative dielectric constant (ε_r) of $KTaO_3$ at 14 K (a) and 60 K (b). Numbers 1 to 5 indicate the sequence of the measurement cycles.

also dependent on the field history. At higher temperature (40 K), the hysteresis disappears.

III. LANDAU-GINZBURG-DEVONSHIRE (LGD) THEORY AND FITTING

The dielectric constant of polar dielectrics changes significantly with the applied external electric field (E), and nonlinear behavior occurs. The phenomenological treatments of the dc electric-field dependence of the dielectric constant in polar dielectrics are currently within the framework of LGD theory.[10–14]

A. LGD free-energy expansion and the approximate treatments

1. LGD theory and two implicit equations for $\varepsilon_r(E)$

According to LGD theory, considering a standard treatment in a strained cubic crystal, the free energy can be written as[1,2]

$$F(P,T)=F(0,T)+\alpha/_{2}P^2+\beta/_{4}P^4+\gamma/_{6}P^6+\cdots, \qquad (1)$$

where $\alpha=C(T-T_0)=1/\varepsilon(0)=1/[\varepsilon_0\varepsilon_r(0)]$ is a temperature-dependent coefficient, C is a constant, T_0 is the Curie-Weiss temperature, $\varepsilon(0)$ is the dielectric constant at zero field, ε_0 is the permittivity of space, $\varepsilon_r(0)$ is the relative dielectric constant at zero field, $\varepsilon(0)=\varepsilon_0\varepsilon_r(0)$, P is polarization, and β and γ are generally temperature-independent coefficients.

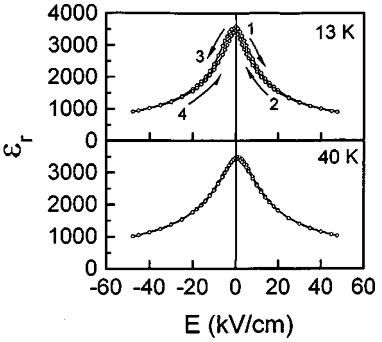

FIG. 2. dc electric-field dependence of the relative dielectric constant (ε_r) of $(Sr_{1-1.5x}Bi_x)TiO_3$ ($x=0.002$) at 13 K (a) and 40 K (b). Numbers 1 to 4 indicate the sequence of the measurement cycles.

We know that

$$\partial F/\partial P=E=\alpha P+\beta P^3+\gamma P^5+\cdots \qquad (2)$$

and we can get

$$\partial E/\partial P\approx 1/(\varepsilon_0\varepsilon_r)=\alpha+3\beta P^2+5\gamma P^4+\cdots. \qquad (3)$$

Equations (2) and (3) provide the relationship between the electric field and the polarization, hence the relationship between the electric field and the dielectric constant. Using Eqs. (2) and (3), we can obtain the field dependence of polarization and dielectric constants, after the parameters α, β, and γ are determined.

Equations (2) and (3) implicitly include the field dependence of the polarization and dielectric constant. Generally speaking, an explicit function rather than an implicit function is preferable for describing the field dependence of the dielectric constant. Due to this preference, several approximate treatments have been developed, as shown below.

2. Johnson's relationship[10]

Johnson's scenario is performed assuming a small polarization,

$$P=\varepsilon_r(E)\varepsilon_0 E. \qquad (4)$$

In the case of small P, neglect terms P^4 and higher in Eq. (3) and substitute Eq. (4) into Eq. (3). For example, if $P\leqslant 1\ \mu C/cm^2=0.01\ C/m^2$, then $P^2\leqslant 1\times 10^{-4}\ (C/m^2)^2$ and $P^4\leqslant 1\times 10^{-8}\ (C/m^2)^4$ as $\beta=\sim 10^{10}\ (V\,m^5/C^3)$ and $\gamma=\sim 10^{12}\ (V\,m^9/C^5)$; in this case, neglecting the P^4 term is reasonable. Thus

$$\begin{aligned}1/(\varepsilon_r\varepsilon_0)&=1/[\varepsilon_r(0)\varepsilon_0]+3\beta(\varepsilon_r\varepsilon_0 E)^2\\&=1/[\varepsilon_r(0)\varepsilon_0]+\lambda(\varepsilon_r\varepsilon_0 E)^2,\end{aligned} \qquad (5)$$

where $\lambda=3\beta$.

Equation (5) can be rewritten as

$$\begin{aligned}\varepsilon_r/\varepsilon_r(0)=&\{1-\varepsilon_r/\varepsilon_r(0)+[\varepsilon_r/\varepsilon_r(0)]^3\}^{1/3}/\\&[1+\lambda\varepsilon_r(0)^3\varepsilon_0^3E^2]^{1/3}.\end{aligned} \qquad (6)$$

Checking the factor $\{1-\varepsilon_r/\varepsilon_r(0)+[\varepsilon_r/\varepsilon_r(0)]^3\}^{1/3}$ for all possible $\varepsilon_r/\varepsilon_r(0)$ values between 0 and 1, it is found that the value of this term is around 1, with the maximum deviation being $\sim$15% at $\varepsilon_r/\varepsilon_r(0)=\sim 0.6$. Thus, a semiempirical relation is obtained,

$$\varepsilon_r(E)=\varepsilon_r(0)/\{1+\lambda[\varepsilon_0\varepsilon_r(0)]^3E^2\}^{1/3}. \qquad (7)$$

Johnson reported that Eq. (7) can be valid for $(Sr,Ba)TiO_3$ in the paraelectric state up to high dc electric field.[10]

It should be pointed out that the relationship Eq. (7) only works when $\beta>0$.

If $\beta<0$, at least the fourth-order term in Eq. (3) must be included, and the approximation can be written as follows:

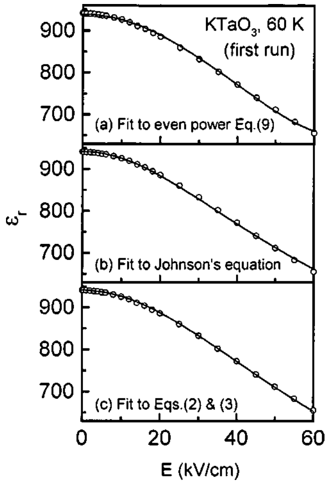

FIG. 3. (a)–(c) Fitting to the dc electric-field dependence of the relative dielectric constant (ε_r) of $KTaO_3$ at 60 K (first run) using the even-power equation (9), Johnson's relation (7), and Eqs. (2) and (3) (symbols, experimental data; solid curves, fitting results).

$$1/(\varepsilon_r\varepsilon_0)=1/[\varepsilon_r(0)\varepsilon_0]+3\beta(\varepsilon_r\varepsilon_0E)^2+5\gamma(\varepsilon_r\varepsilon_0E)^4. \tag{8}$$

Solving this implicit equation, we can obtain the dielectric constant as a function of electric field.

3. Even-power relation at low fields

For the Johnson relation, a prerequisite $\lambda\varepsilon(0)^3E^2<1$ can be met in most practical cases. For example, for $KTaO_3$ and $SrTiO_3$, $\lambda=3\beta=\sim10^{10}$ $(\mathrm{V\,m^5/C^3})$,[14] and the relative permittivity $\varepsilon_r(0)\leqslant1000$, then $\lambda[\varepsilon_0\varepsilon_r(0)]^3E^2\leqslant0.007$ at $E\leqslant10$ kV/cm, and $\lambda[\varepsilon_0\varepsilon_r(0)]^3E^2\leqslant0.25$ at $E\leqslant60$ kV/cm. Hence, Johnson relation Eq. (7) can be expanded as a polynomial consisting of even-power terms of E to high orders,

$$\varepsilon_r(E)=\varepsilon_r(0)/\{1+\lambda[\varepsilon_0\varepsilon_r(0)]^3E^2\}^{1/3}=\varepsilon_1-\varepsilon_2E^2+\varepsilon_3E^4-\varepsilon_4E^6+\varepsilon_5E^8-\cdots,$$

where $\varepsilon_1=\varepsilon_r(0)$, $\varepsilon_2=\frac{1}{3}\lambda\varepsilon(0)^4$, $\varepsilon_3=\frac{2}{9}\lambda^2\varepsilon(0)^7$, $\varepsilon_4=\frac{14}{81}\lambda^3\varepsilon(0)^{10}$, $\varepsilon_5=\frac{35}{243}\lambda^4\varepsilon(0)^{13}$, etc.

In fact, the even-power relation

$$\varepsilon_r(E)=\varepsilon_1-\varepsilon_2E^2+\varepsilon_3E^4-\varepsilon_4E^6+\varepsilon_5E^8-\cdots \tag{9}$$

is a common relationship for analyzing the electric-field dependence of the dielectric constant in the literature. It should be emphasized that this treatment is strictly limited to (i) a small dc electric field and (ii) a small polarization case (near-paraelectric state). Under these two prerequisites, Eq. (9) describes the dielectric constant under dc electric field for many materials.

B. Fitting results for paraelectric $KTaO_3$

1. Paraelectric $KTaO_3$

For the data with a relatively smaller dielectric constant $[\varepsilon_r(0)=\sim1000]$ at 60 K, the fitting to the even-power Eq. (9) and Johnson's relation [Eq. (7)] is shown in Figs. 3(a) and 3(b) from 0 to 60 kV/cm. The fitting looks reasonable and there is not much difference for the fitting between the two equations. The fitting parameters are $\varepsilon_1=938$, $\varepsilon_2=1.27\times10^{-11}$ $(\mathrm{V/m})^{-2}$, and $\varepsilon_3=1.38\times10^{-25}$ $(\mathrm{V/m})^{-4}$ for the even-power term Eq. (9); $\lambda=3\beta$, $\beta=3.010^{10}$, $(\mathrm{V\,m^5/C^3})$ for Johnson's relation.

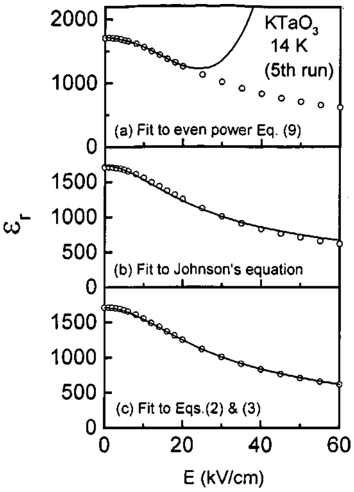

FIG. 4. (a)–(c) Fitting to the dc electric-field dependence of the relative dielectric constant (ε_r) of $KTaO_3$ (the fifth run) at 14 K using the even-power equation (9), Johnson's relation (7), and Eqs. (2) and (3) (symbols, experimental data; solid lines, fitting results).

The fitting to the data for *the fifth run at 14 K* with a higher ε_r shows that the even-power relation seems only reasonable below 20 kV/cm, as shown in Fig. 4(a); but the fitting with Johnson's relation [Eq. (7)] is more reasonable up to 60 kV/cm, as shown in Fig. 4(b). The fitting parameters are $\varepsilon_1=1716$, $\varepsilon_2=1.71\times10^{-10}$ $(\mathrm{V/m})^{-2}$, and $\varepsilon_3=1.39\times10^{-23}$ $(\mathrm{V/m})^{-4}$ for the even-power term Eq. (9); $\lambda=3\beta,\beta=4.23\times10^{10}$ $(\mathrm{V\,m^5/C^3})$ for Johnson's relation.

For the dielectric data obtained at *the first run at 14 K* with an even higher $\varepsilon_r(0)$ (~2800) for paraelectric $KTaO_3$, the even-power relation fitting is only reasonable below ~10 kV/cm, as shown in Fig. 5(a). The fitting to Johnson's relation is reasonable up to 60 kV/cm, but with a large fitting error, as shown in Fig. 5(b). The fitting parameters are $\varepsilon_1=2761$, $\varepsilon_2=7.24\times10^{-10}$ $(\mathrm{V/m})^{-2}$, and $\varepsilon_3=9.78\times10^{-23}$ $(\mathrm{V/m})^{-4}$ for the even-power term; $\lambda=3\beta,\beta=3.8\times10^{10}$ $(\mathrm{V\,m^5/C^3})$ for Johnson's relation.

2. Limitation of the approximate treatments

The fitting results show that the even-power Eq. (9) only works for a low dielectric constant and at low electric fields. This is not surprising because Eq. (9) is assumed to hold only for low electric fields and small polarizations.

Johnson reported that Eq. (7) can describe the dielectric behavior of $(Sr,Ba)TiO_3$ up to a high dc electric field (40 kV/cm).[10] In the present work, the experimental data from paraelectric $KTaO_3$ can be described by the Johnson relation Eq. (7), but the accuracy for the case of a high dielectric constant is not satisfactory.

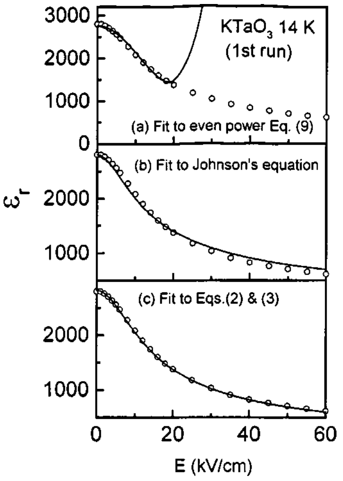

FIG. 5. (a)–(c) Fitting to the dc electric-field dependence of the relative dielectric constant (ε_r) of $KTaO_3$ (the first run) at 14 K using the even-power equation (9), Johnson's relation (7), and Eqs. (2) and (3) (symbols, experimental data; solid lines, fitting results).

3. Fitting with the LGD implicit equations (2) and (3)

As mentioned above, Eqs. (2) and (3) include all information on the relationship between the polarization and electric field. With the development of computational programs and personal computers in recent years, the nonlinear equations (2) and (3) can be conveniently solved by ignoring higher-order terms (sixth and higher). Our nonlinear fitting results of the field dependence of the dielectric constant for $KTaO_3$ are shown in Figs. 3(c), 4(c), and 5(c). Good agreement between the experimental data and the fitting curves has been obtained. The parameters used, $\beta = 10^{10}$ $(\mathrm{V\,m^5/C^3})$, $\gamma = 10^{11}$ $(\mathrm{V\,m^9/C^5})$, are from the literature.[14]

Equations (2) and (3) are good enough to describe the electric-field dependence of the dielectric constant up to high fields. The traditional approximate treatment with the even-power relationship is only a rough approximation for the dielectric response at low electric fields. Although Johnson's relation could be an approximate expression up to high field, its accuracy is less than that of Eqs. (2) and (3).

4. Possible existence of two polarization mechanisms in $KTaO_3$

Although the fitting curves for $KTaO_3$ by the LGD theory [Eqs. (2) and (3)] or the approximate relationship Eq. (7) are in good agreement with the experimental data, a question is raised as to whether this fitting reflects the real physical nature of the polarization.

The results in Fig. 1 show that the electric-field dependence of $KTaO_3$ at 14 K is strongly dependent on the electric-field history. After the first run to the maximum electric field of 60 kV/cm, the dielectric constant $\varepsilon_r(0)$ is not recovered to its original value of a virgin state after the electric field is decreased to zero at the end of the second run. In the following third to fifth runs, $\varepsilon_r(0)$ still decreases until at the sixth run a stable value is attained.

The larger difference in the dielectric constant at low bias levels between different cycles implies the existence of some entities which can be easily polarized and aligned along the dc bias direction. Even after removal of the bias, the original state is not fully recovered during the short measurement time (several hours), and thus the weak signal dielectric response $\varepsilon_r(0)$ at zero bias field is lowered. After more cycles, all these entities seem to be fully polarized (aligned) and tend to be stable, and the dielectric constant remains almost the same at zero field, but at a much lower value than that of the original state.

What is the physical nature of these easily polarized entities? Similar phenomena observed in ferroelectric materials were attributed to polarization of domain walls and/or other defects.[15] It is well known that there is no macrodomain in paraelectric $KTaO_3$, but it is also reported that some nanoclusters exist whose size increases with decreasing temperature.[16] Based on this, it is reasonable to assume that the entities are very probably the nanocluster walls/boundaries. In addition, this orientational effect under dc bias at a low temperature (14 K) is more pronounced than at a high temperature, which further supports this hypothesis. If so, two types of polarization contributions occur in $KTaO_3$, at least at very low temperatures. Although Eqs. (2) and (3) mathematically provide reasonable fitting to the dielectric constant of $KTaO_3$ under dc fields [Figs. 3(c), 4(c), and 5(c)], its physical meaning is unclear (see further discussion below). This is why a cluster polarization term was taken into account for describing the field dependence of the dielectric constant for $KTaO_3$ in Ref. 17.

IV. MULTIPOLARIZATION-MECHANISM MODEL

A. Analysis of the structure of polarization spectra in polar dielectrics

It should be emphasized that all the above fittings are obtained under a precondition that *only one polarization mechanism* is taken into consideration in the materials. However, there is more than one polarization mechanism in many practical cases, i.e., two or more polarization mechanisms generally coexist in a material.

For $Bi:SrTiO_3$,[6] it was demonstrated that there are two "dielectric relaxor" modes superimposed on the quantum paraelectric background (QPB) of $SrTiO_3$. The temperature dependence of the relative dielectric constant for $Bi:SrTiO_3$ is replotted in Fig. 6. The "dielectric relaxor" modes are induced by the off-centered Bi dipoles. Based on this observation, it can be recognized that the field dependence of the relative dielectric constant shown in Fig. 2 is composed of three contributions at zero field: one from mode *A*, another

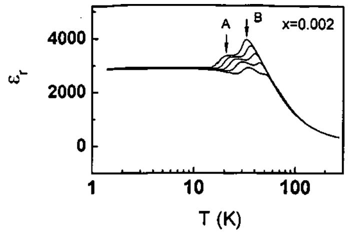

FIG. 6. Temperature dependence of the relative dielectric constant (ε_r) of $(Sr_{1-1.5x}Bi_x)TiO_3$ ($x = 0.002$) at 0.1, 1, 10, 100, and 1000 kHz (from top to bottom).

from mode B, and the rest of the dielectric constant from the QPB of $SrTiO_3$. Under dc bias, the two dielectric modes are easily suppressed, while the dielectric background sustained under high dc bias, although decreased, is from more "intrinsic" QPB contributions.[6,18] Thus the field dependence of the dielectric constant at a certain temperature reflects such a multipolarization mechanism. Therefore, the field dependence of the dielectric constant of $Bi:SrTiO_3$ cannot be described by the single polarization mechanism using Eqs. (2) and (3), or the approximate treatments Eq. (7) and Eq. (9).

This is reminiscent of the dielectric response in the ferroelectric state of PZT at room temperature, which has been recognized as containing both intrinsic and extrinsic contributions.[15] Moreover, polar clusters are reported to be superimposed on a paraelectric background. For instance, the dielectric temperature spectra of SbSI can be decomposed into a dielectric peak superimposed on a so-called quantum paraelectric background under pressure.[19]

On the other hand, recent efforts on applying LGD theory to a ferroelectric relaxor seem rather difficult,[20] although the theory has been successfully applied to the description of $BaTiO_3$ (Ref. 21) and $Pb(Zr,Ti)O_3$.[22] This might be mainly due to the existence of some nanopolar clusters in the ferroelectric relaxor, which are superimposed on the dielectric/ferroelectric polarization background of the material. The single polarization mechanism is found to be insufficient to describe the whole polarization picture.

Therefore, the dielectric spectra observed in polar dielectrics, including paraelectrics, ferroelectrics, and ferroelectric relaxors, may generally include many possible polarization contributions from different polarization mechanisms.[23] The schematic diagrams of the structure of the dielectric spectra of these three types of polar dielectrics are summarized in Fig. 7. For paraelectric and dielectric relaxors, the structure of dielectric temperature spectra consists of the paraelectric background and possible micropolar-cluster walls.

One typical example of ferroelectrics is the dielectric spectrum of the ferroelectric and ferroelastic $Cd_2Nb_2O_7$ as reported in Ref. 24. Around the paraelectric-ferroelectric phase-transition temperature, the dielectric spectrum consists of polarization contributions from electrons, phonons, ferroelectric-ferroelastic effect, ferroelectric macrodomain-wall motions, polar microclusters, etc. At a fixed temperature, the dielectric constant is gradually suppressed with increasing dc bias due to the different response of these polarization mechanisms at different bias levels. Thus, multipolarization mechanisms are reflected in the $\varepsilon_r(E)$ profile.

For the ferroelectric relaxor, in addition to the electron, phonon, and the polar microcluster contributions, the polar microcluster wall motions may become important at low frequencies.

In addition, in the so-called soft-mode dielectrics, such as $SrTiO_3$ and $KTaO_3$, the possible coupling between unavoidable defects/impurities and the soft mode may lead to a large contribution to the dielectric constant. The possible existence of microclusters and their wall motion may greatly enhance the dielectric constant. In a material with more than one polarization mechanism, fitting using single-polarization-mechanism equations, like Eqs. (2) and (3), makes no sense physically, although fitting may be in good agreement with the experimental data because Eqs. (2) and (3) are infinite series in mathematics, and the combination of these two equations can provide a powerful fitting regardless of any physical mechanisms or details.

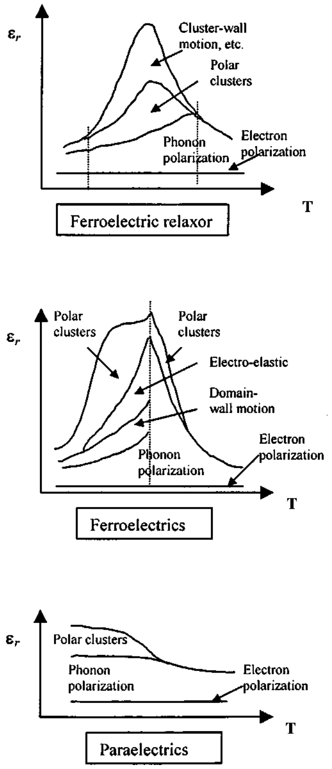

FIG. 7. Schematic diagrams of the temperature dependence of polarization species for ferroelectric relaxors, ferroelectrics, and paraelectrics.

B. Description of the "extrinsic" polarization mechanism

According to the above analysis of dielectric spectra, a question is how to describe the field dependence of the dielectric constant in polar dielectrics with more than one polarization mechanism. One scenario is using two sets of order parameters, for example for the LGD free-energy expansion,

$$F(P,T)=F(0,T)+\alpha_1/_2P_1^2+\beta_1/_4P_1^4+\gamma_1/_6P_1^6+\alpha_2/_2P_2^2 +\beta_2/_4P_2^4+\gamma_2/_6P_2^6+\cdots. \tag{10}$$

The parameters P_1 and P_2 represent two order parameters. More terms may be added when considering the interaction between the two order parameters.

An alternative scenario is to decompose the different polarization mechanisms and to describe their contributions, respectively. As is discussed above, it is observed that there is more than one polarization contribution to the dielectric response for many nonlinear polar dielectrics. One comes from an intrinsic contribution of the lattice phonon polarization, which can be described by the principal order parameters of the phenomenological theory. The other comes from some ‘‘extrinsic’’ polarization contributions, such as domain-wall motions, nanometer polar clusters, and phase boundary polarization.

Generally, the ‘‘extrinsic’’ polarization contribution exhibits some common characteristics summarized as (i) the dielectric constant is suppressed quickly with increasing dc electric fields, and (ii) the dielectric constant decreases quickly with increasing frequencies. These characteristics seem indicative of the behavior of a ‘‘reorientation polarization’’ mechanism.

In fact, we could deal with ‘‘extrinsic’’ polarizations as ‘‘reorientation polarization of dipoles’’ using the following assumptions and approximations.

(i) All clusters have the same size (or volume V).

(ii) All clusters have the same polarization P_0, which depends on temperatures.

(iii) Cluster activation energies are at the level of temperature fluctuations, and these fluctuations can reorient the polar clusters.

In this case, *we recognize the cluster as a giant dipole*. In dielectric physics, we have a standard treatment to deal with the reorientation polarization of dipoles.[4] The average electric moment along the dc electric-field direction is

$$\langle \mu_{\text{average}} \rangle = \mu_0 [\coth(\mu_0 E/k_B T) - 1/(\mu_0 E/k_B T)] = \mu_0 L(\mu_0 E/k_B T), \tag{11}$$

where $L(\mu_0 E/k_B T)$ is the Langevin function, μ_0 is the electric moment of the dipoles, and k_B is Boltzmann’s constant. As mentioned above, *we assume the cluster is a giant dipole*, that is, we can simply substitute $\mu_0 = P_0 V$ into Eq. (11), and obtain the total polarization of the cluster system under dc bias,

$$P = \langle P_{\text{average}} \rangle = P_0 [\coth(P_0 VE/k_B T) - k_B T/P_0 VE]. \tag{12}$$

Thus, the dielectric constant is derived as

$$\varepsilon = \partial P/\partial E,$$

$$\varepsilon_r = (P_0 x/\varepsilon_0)[1/(xE)^2 - 1/\sinh^2(Ex)], \tag{13}$$

where $x = P_0 V/k_B T$.

A similar relationship can also be derived from the ‘‘double-well’’ model for the reorientational polarization,[5]

$$\mu = \mu_0 \tanh(\mu_0 E_{\text{eff}}/k_B T). \tag{14}$$

The effective field is $E_{\text{eff}} = E + \eta P$, where η is a generalized Lorentz factor depending on the geometry of the dipole lattice. Generally speaking, P is small for the ‘‘extrinsic polarization,’’ and we have an approximation $E_{\text{eff}} = E$. Then Eq. (14) can be rewritten as

$$P = P_0 \tanh(\mu_0 E/k_B T) = P_0 \tanh(P_0 VE/k_B T), \tag{15}$$

where P_0 is the effective polarization of one cluster.

Based on Eq. (15), the dielectric constant is derived as

$$\varepsilon = \partial P/\partial E,$$

$$\varepsilon_r = (P_0 x/\varepsilon_0)[\cosh(Ex)]^{-2}, \tag{16}$$

where $x = P_0 V/k_B T$.

In the literature, Eqs. (15) and (16) were used by Bell[25] in dealing with ferroelectric-relaxor behavior, and also by Bianchi *et al.*[26] and Chen *et al.*[17] in describing the dc field dependence of the dielectric constant.

It should be pointed out that there is no significant difference between Eq. (13) and Eq. (16) in electric-field dependence of the dielectric constant. In this work, we use Eq. (16) due to its simplicity. It should be pointed out that when E is small, Eq. (16) can also be simplified to an even-power polynomial, Eq. (9) (see the Appendix).

C. Multipolarization-mechanism model

When two or more polarization mechanisms coexist in a polar dielectric, a combination of different polarization contributions should be taken into consideration. In the present work, a *multipolarization-mechanism* model is proposed to describe the dielectric response of a polar dielectric under dc bias by combining the intrinsic contribution with the extrinsic contribution as a reorientation polarization.

The above results show that the semiempirical Johnson’s relation Eq. (7) is a reasonable approximation of LGD phenomenological theory [Eqs. (2) and (3)] for describing the dielectric behavior under dc fields. Therefore Eq. (7) is used to describe the contribution of the lattice polarization. Equation (16) is used to describe the ‘‘reorientation polarization’’ mechanism. A combined equation of the Johnson relation Eq. (7) and the cluster-polarization contribution Eq. (16) is therefore adopted,

$$\varepsilon_r(E) = \varepsilon_r(0)/\{1 + \lambda[\varepsilon_0 \varepsilon_r(0)]^3 E^2\}^{1/3} + \Sigma (P_0 x/\varepsilon_0) \times [\cosh(Ex)]^{-2}, \tag{17}$$

where Σ means the sum over different cluster-polarization terms. In many cases, one term is sufficient, however in a complicated case, two or three cluster-polarization terms may be taken into account to describe the dielectric response.

D. Fitting of the dielectric behavior of Bi:SrTiO$_3$ and KTaO$_3$ under dc bias

Bi:SrTiO$_3$

Two cluster terms are used in Eq. (17) due to the two polarization mechanisms modes A and B superimposed on the quantum paraelectric background. The fitting to experimental data using Eq. (17) at several temperatures is shown in Fig. 8. It can be seen that the fitting curves (solid lines) are in good agreement with the experimental data in Fig. 8. From the fitting, β is in the range from $\sim 1.5 \times 10^{10}$ to 2.7×10^{10} (V m^5/C^3) in the temperature range of 13–65 K; this is in good agreement with the data reported in Ref. 14.

From Fig. 8, the polar clusters contribute significantly to the dielectric constant up to ~20 kV/cm for both clusters A and B. Without dc bias, the contribution to the dielectric constant is about 24% for cluster B (mode B) at 40 K around which mode B reaches its maximum in the ε_r versus T profile, and the contribution to the dielectric constant is ~16%

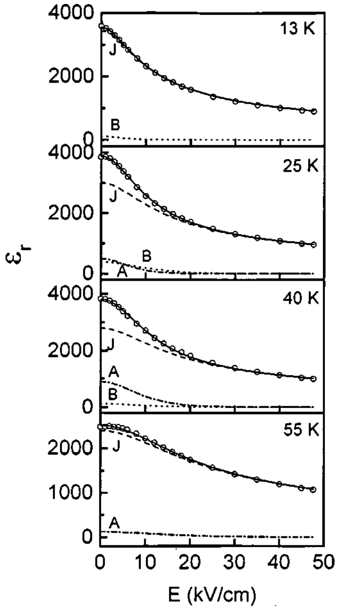

FIG. 8. Electric-field dependence of the dielectric constant (ε_r) of Bi:SrTiO$_3$ at 13, 25, 40, and 55 K at 10 kHz. Open circles, experimental data; solid lines, fitting results according to Eq. (17) including the contribution from the Johnson term *J* (dash line), the contribution from cluster *A* (dash-dot), and that from cluster *B* (dot).

for cluster *A* (mode *A*) at 25 K around which mode *A* reaches its maximum in the ε_r versus *T* profile.

The cluster polarizations of the two polar clusters corresponding to modes *A* and *B* obtained by fitting to Eq. (17) are shown in Fig. 9. It can be seen that clusters *A* and *B* reach their maximum at 25 and 40 K, respectively, with polarizations $P_A = 0.39\ \mu\text{C/cm}^2$ and $P_B = 0.80\ \mu\text{C/cm}^2$, which correspond to the temperature at which ε_r maximum occurs. It is interesting to notice that slim hysteresis loops are observed for this sample although it acts as a "dielectric relaxor".[6] The remnant polarization is of ~0.2, 0.6, and 1.2 μC/cm^2 at 10, 20, and 30 kV/cm, respectively. The cluster polarization values obtained from the calculation by Eq. (17) are comparable to these measured data within the same order of magnitude. The calculated size of the polar cluster is ~4–7.5 nm for both modes *A* and *B* in the whole tempera-ture range, which is also in the same order of magnitude as observed in Ca-doped SrTiO$_3$.[26]

KTaO$_3$

The fitting to the experimental data at the first and fifth runs using Eq. (17) *with one polar cluster term* is shown in Fig. 10. It can be seen that the fitting curves (solid lines) fit well to the experimental data. For Johnson's term, β is $\sim 5.5\times 10^{10}$ (V m^5/C^3) for both cases. The cluster size of 2.5 nm at the first run decreases down to 2.1 nm at the fifth run for the cluster term, which is in good agreement with the size of five to six unit cells (~2–3 nm) of ferroelectric microregions suggested by the study of Raman spectra in Ref. 16. The polar-cluster polarization of ~0.7 μC/cm^2 is obtained for both runs.

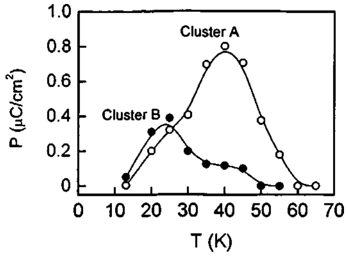

FIG. 9. Temperature dependence of the polar-cluster polarization (*P*) for clusters *A* and *B* obtained by the best fit to the dc electric-field dependence of the dielectric constant to Eq. (17).

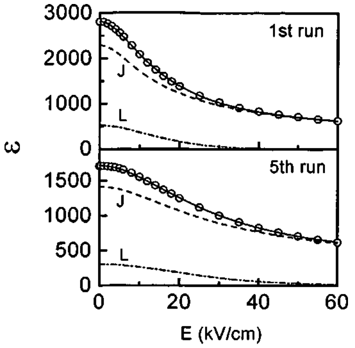

FIG. 10. Electric-field dependence of the dielectric constant (ε_r) of KTaO$_3$ at 14 K for the first and fifth run. Open circles, experimental data; solid lines, fitting results according to Eq. (17) including the contribution from the Johnson term *J* (dash line) and the contribution from the cluster term *L* (dash-dot).

Although the fitting data by using Eq. (17) are similar to those results reported in Ref. 17, where a combination of the even-power equation and the cluster term was used, Eq. (17) in the present work is more physically reasonable for the fitting because of the limitation of the validation of the even-power equation at high electric fields.

V. CONCLUSIONS

The theoretical treatment of Landau-Ginzburg-Devonshire (LGD) theory and its approximate treatments of the electric-field dependence of the dielectric constant in polar dielectrics are discussed. It is found that a treatment of LGD-group equations (2) and (3) can describe the field dependence of the dielectric constant very well for a single-polarization-mechanism process. On the other hand, the semiempirical Johnson relation (7), which is an explicit function of the electric field, is a reasonable approximate description for the field dependence of the dielectric constant in replacing the rigorous theoretical treatment in many cases.

Furthermore, based on the empirical observation of the structure of dielectric spectra, multipolarization processes occur in many polar dielectrics. In this case, the treatment based on a single order parameter of LGD theory is insufficient. A multipolarization-mechanism model is therefore suggested in the present work, and

$$\varepsilon_r(E) = \varepsilon_r(0)/\{1+\lambda[\varepsilon_0\varepsilon_r(0)]^3E^2\}^{1/3} + \Sigma(P_0x/\varepsilon_0)[\cosh(Ex)]^{-2}$$

is adopted to describe the field dependence of the dielectric constant, where Johnson's term represents the lattice polarization induced from the LGD theory, and the latter represents the reorientational polarization contribution. The fitting to experimental data shows that the proposed multipolarization-process model works well.

It should also be mentioned that the Johnson relationship $\varepsilon_r(0)/\{1+\lambda[\varepsilon_0\varepsilon_r(0)]^3E^2\}^{1/3}$ and the reorientation polarization term $(P_0x/\varepsilon_0)[\cosh(Ex)]^{-2}$ can also be simplified to even-power polynomials when the electric field and/or dielectric constant is small.

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APPENDIX

Now let us consider the cluster polarization relation Eq. (16). In most cases, a precondition, $xE=(P_0V/k_BT)E\ll 1$, can be realized. For example, as $P_0=1\ \mu\mathrm{C/cm^2}=0.01\ \mathrm{C/m^2}$, $V=10\ \mathrm{nm^3}$, and $k_BT=0.026$ eV at 300 K, we have $x=2.4\times10^{-8}$ m/V. For $E=10\ \mathrm{kV/cm}=10^5$ V/m, $xE=2.4\times10^{-3}\ll 1$. Thus the relationship can be simplified as

$$(P_0x/\varepsilon_0)[\cosh(Ex)]^{-2}=(P_0x/\varepsilon_0)[1+(Ex)^2/2]^{-2}. \tag{A1a}$$

Obviously, the condition $(Ex)^2/2<1$ is also satisfied, and Eq. (A1a) can be written in an expanded form,

$$\begin{aligned}(P_0x/\varepsilon_0)&[1+(Ex)^2/2]^{-2}\\ &=(P_0x/\varepsilon_0)[1-2(Ex)^2/2+3(Ex)^4/4-4(Ex)^6/8\\ &\quad+5(Ex)^8/16-\cdots]\\ &=q_1-q_2E^2+q_3E^4-q_4E^6+q_5E^8-\cdots\end{aligned} \tag{A1b}$$

where $q_1=(P_0x/\varepsilon_0)$, $q_2=P_0x^3/\varepsilon_0$, $q_3=\frac{3}{4}P_0x^5/\varepsilon_0$, $q_4=\frac{1}{2}P_0x^7/\varepsilon_0$, $q_5=\frac{5}{16}P_0x^9/\varepsilon_0$, etc. Equation (16) also includes all even-power terms, as does Eq. (9).

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