

Cluster polarization of $\text{Cd}_2\text{Nb}_2\text{O}_7$ compound

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The direct-current (dc) electric-field dependence of dielectric constant around paraelectric–ferroelectric transition in $\text{Cd}_2\text{Nb}_2\text{O}_7$ has been studied. The results show significant suppression of the dielectric constant by the application of dc bias. The electric-field dependence of the dielectric constant at the temperature around paraelectric–ferroelectric phase transition can be well described by the modified Devonshire relation including a cluster term, i.e., $\epsilon(E) = \epsilon_1 - \epsilon_2 E^2 + \epsilon_3 E^4 + (Px/\epsilon_0)[\cosh(Ex)]^{-2}$. The fit parameters indicate that the polar-cluster carries polarization $P = \sim 0.5\text{--}2.5 \text{ mC/m}^2$ with the cluster size of $L = \sim 11\text{--}15 \text{ nm}$. © 2000 American Institute of Physics. [S0003-6951(00)04531-9]

The dielectric behavior of cadmium pyroniobate $\text{Cd}_2\text{Nb}_2\text{O}_7$ shows “unusual properties.” It is reported that there are up to possible eight phase transitions in the temperature range of 10–300 K, detected by dielectric, light scattering, electro-optic, and specific heat measurements in $\text{Cd}_2\text{Nb}_2\text{O}_7$.^{1–18} In a narrow temperature range of 170–205 K, $\text{Cd}_2\text{Nb}_2\text{O}_7$ displays three dielectric anomalies, at $\sim 177\text{--}185$, 196–201, and 201–205 K.¹⁹ The dielectric anomalies were classified as (1) an improper paraelastic–ferroelastic and an improper paraelectric–ferroelectric phase transition at 201–205 K, (2) a sharp paraelectric–ferroelectric phase transition at 196–201 K (hereafter denoted as peak A), and (3) a “diffuse ferroelectric transition” at 177–185 K (denoted as mode I), whose T_m (the temperature of the dielectric constant maximum) apparently increased with increasing electric field.^{5–14} However, clear understanding of transitions is still not available because of the complicated series of close-by transitions.

Recently, the present authors have studied electric-field dependence of the dielectric behavior, and found that the T_m of the mode I is independent of the electric field.²⁰ This does not support the hypothesis of “diffuse ferroelectric transition,” because it is known that, for diffuse ferroelectric transition, the T_m is electric-field dependent, and follows the de Almeida–Thouless relationship.^{21,22} In this letter, we reported further study on the dc electric-field dependence of this dielectric mode.

The ceramic samples of $\text{Cd}_2\text{Nb}_2\text{O}_7$ were prepared by the solid state reaction. Complex dielectric permittivity was measured using a HP 4284A LCR Meter with an alternating-current (ac) field of 2 V/mm. The temperature dependence of dielectric constant was measured in a cryostat system, while the specimen was being cooled or heated up with or without constant direct-current (dc) bias. The electric-field dependence of the dielectric constant was measured at a fixed temperature, at which the sample was allowed to reach thermal equilibration for 15–30 min before the measurement. The dc voltage was applied to the samples and a blocking circuit was adopted to separate the high dc voltage and LCR meters.

The temperature dependence of the dielectric constant (ϵ) for $\text{Cd}_2\text{Nb}_2\text{O}_7$ measured in heating and cooling cycle is shown in Figs. 1(a) and 1(b), respectively. For the cooling cycle, without dc bias, in the temperature range of 160–220 K, there are two dielectric anomalies, mode I at $\sim 178 \text{ K}$, and peak A at $\sim 195 \text{ K}$. As mentioned above, peak A has been assigned as a ferroelectric–paraelectric phase transition, and mode I has been assigned as a diffuse ferroelectric phase transition in the earlier literature.^{3–6,14,17} Under dc bias, for example, at 3 kV/cm, mode I is greatly suppressed, and peak A dominates. At the heating cycle, as shown in Fig. 1(b), mode I at $\sim 178 \text{ K}$ is obvious, peak A only shows the small difference in the changing rate of ϵ with decreasing temperature (an anomaly could be seen in the temperature dependence of the $1/\epsilon$). It should be pointed out that the dielectric constant maximum and its temperature obtained at the heat-

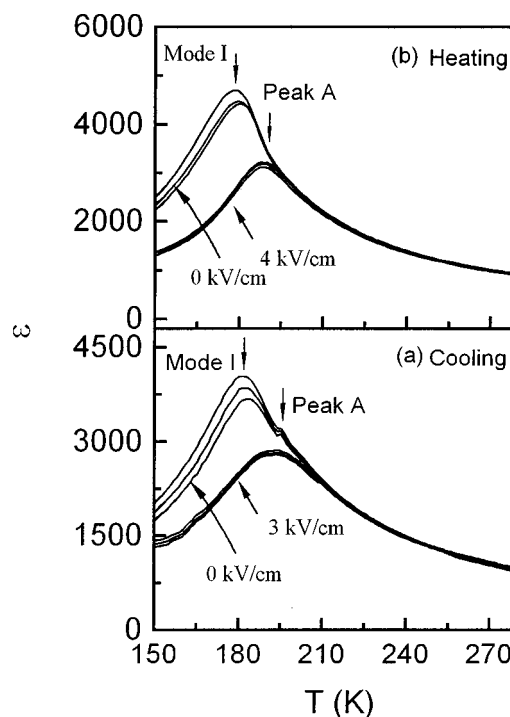


FIG. 1. Temperature dependence of ϵ in the temperature range of the paraelectric–ferroelectric phase transition measured in (a) the cooling cycle and (b) the heating cycle (from top to bottom, 1, 10, and 100 kHz).

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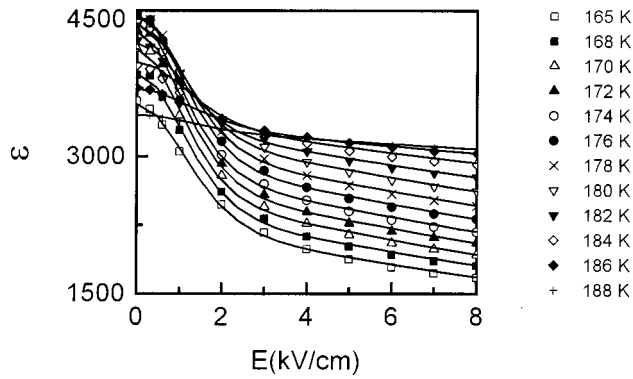


FIG. 2. The dc electric-field dependence of dielectric constant at 5 kHz at the temperatures around the paraelectric–ferroelectric transition. The symbols: experimental data; the solid curves: the fits to Eq. (3).

ing and cooling cycles are slightly different; this is similar to those reported in the literature.^{13,14}

In this work, we focus on the dc electric-field (E) dependence of mode I and peak A. The electric-field dependence of the dielectric constant up to 8 kV/cm at the temperatures around these two dielectric anomalies is shown in Fig. 2. According to the traditional thermodynamics theory,^{23,24} the electric-field dependence of the dielectric constant in the paraelectric state can be expressed as

$$\varepsilon(E) = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4, \quad (1)$$

where ε_1 , ε_2 , and ε_3 are the linear, nonlinear, and high order dielectric constant, respectively. However, in the present work, the poor fits of $\varepsilon(E)$ vs E above T_c by using Eq. (1) indicated that the conventional analysis of ε vs E involving merely even powers of E is not enough to explain the semibell-shaped curves in Fig. 2. The deviation from Eq. (1) implied that there is an excess contribution beyond the paraelectric matrix.

According to the method which was adopted to analyze the field dependence of the dielectric constant in Ca doped SrTiO₃ by Bianchi *et al.*,²⁵ a cluster term was considered as an additional contribution. By means of the Langevin-type approach, the total polarization of a cluster system can be expressed as

$$P_c = P_r \tanh(P_r L^3 E / 2k_B T), \quad (2)$$

with the effective polarization of one cluster P_r , the cluster size L , the electric field E , and Boltzmann's constant k_B . Therefore, the following equation is adopted to analysis the data:

$$\varepsilon(E) = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4 + (P_x / \varepsilon_0) [\cosh(Ex)]^{-2}, \quad (3)$$

where $x = PL^3 / (2k_B T)$ with the cluster polarization P and diameters L . $\varepsilon_{1,2,3}$ and ε_0 designate the linear, nonlinear, and high-order dielectric constant and that of vacuum, respectively. The three leading terms of the right side in Eq. (3) describe the conventional linear and nonlinear response up to the order of E^4 . They correspond to the conventional electric-field dependence of ε of displacive-type polar system in the paraelectric regime, the same as Eq. (1). The fourth term of the right side in Eq. (3) describes the contribution from the possible polar clusters. It can be seen from Fig. 2 that the fitting curves (solid lines) are in good agree-

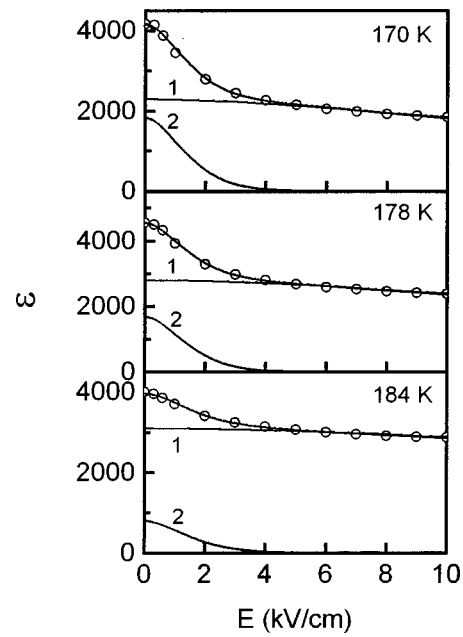


FIG. 3. The dc electric-field dependence of dielectric constant at 170, 178, and 184 K. The symbols: experimental data; the solid curves: the fits to Eq. (3); curve 1 is the contribution from the conventional polarization terms; and curve 2 is the contribution from the polar-cluster term.

ment with the experimental data at the temperatures around the paraelectric–ferroelectric phase transition from 165 to 188 K.

The detailed fitting curves at three typical temperatures are shown in Fig. 3. It can be seen that the contribution of the polar clusters to the permittivity without dc bias is about 45% at 170 K (at the temperature side of the paraelectric–ferroelectric phase transition). At 180 K, near ferroelectric phase transition, the contribution is about 37%. These polar clusters give significant contribution to ε below ~ 4 kV/cm, while, the contribution from the clusters disappears at high electric fields (>5 kV/cm). At 184 K, slightly higher than the T_m , but still in the region of the phase transition, the contribution from the polar clusters decreases to about 20% without dc bias.

The obtained parameters ε_1 , ε_2 , and ε_3 as a function of temperature are shown in Fig. 4(a). The temperature dependence of the linear permittivity ε_1 and nonlinear terms ε_2 and ε_3 reveals that a peak occurs at 180–188 K, the same as the one observed in zero-field permittivity. The size and polarization of the polar clusters are obtained and shown in Fig. 4(b). Below $T \sim 185$ K, the polar clusters carry polarization $P \sim 0.5$ – 2.5 mC/m² and the cluster size, $L \sim 11$ – 15 nm.

What type of polar cluster existed in this compound? Salaev *et al.*¹⁶ and Kolpakova *et al.*¹⁵ reported that ferroelectric and/or ferroelastic domains appear around ~ 205 K, and a change in the domain structure at ~ 200 , ~ 192 , and ~ 178 K. This indicates the complicated domain structure and the motion of domain walls in Cd₂Nb₂O₇. Mode I only present at the ferroelectric state. The straightforward explanation is that mode I results from the motion of the domain walls. However, as mentioned above, recently the present authors found that the T_m of mode I is independent of the electric field,²⁰

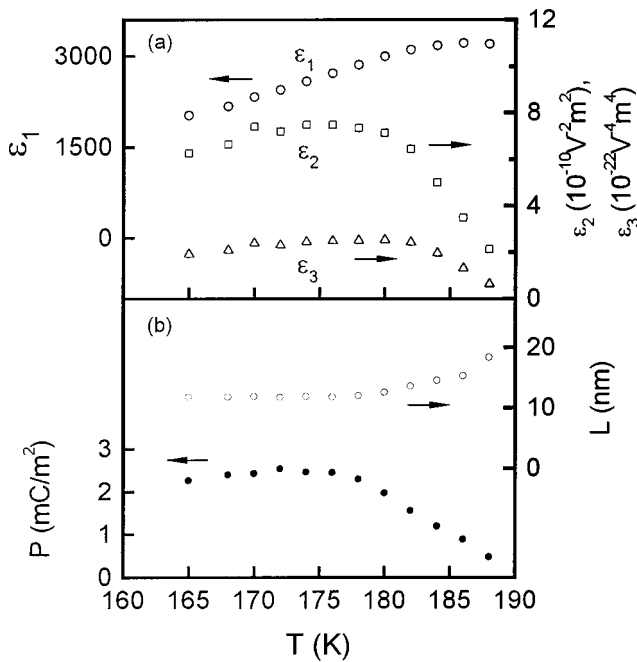


FIG. 4. (a) Temperature dependence of the linear permittivity ϵ_1 and non-linear terms ϵ_2 and ϵ_3 ; (b) Temperature dependence of the polar-cluster polarization (P) and the correlation length (L); obtained by the best fits of dc electric-field dependence.

this indicates that the explanation that the domain walls motion causes the mode I needs more examination.

On the other hand, Kolpakova *et al.*¹⁷ pointed out that because of the special structural characteristics of $\text{Cd}_2\text{Nb}_2\text{O}_7$, the “seventh” oxygen ions are bound only to the cations in the $(\text{NbO}_8)^n$ polyhedra and are not incorporated in the $(\text{NbO}_6)^n$ octahedra, which form the structural framework of the lattice. The reorientation of the seventh oxygen with Cd dipoles under ac external electric fields, will cause the dielectric relaxation.¹⁷ This is similar to those of “defect modes” in Bi doped SrTiO_3 .^{26,27} In the present work, it is possible that the seventh oxygen—Cd dipoles form the polar clusters, and thus contribute to mode I. At this stage, a definite conclusion cannot be reached, and the further work is needed.

In conclusion, the electric-field effect on the dielectric constant at the temperatures around paraelectric–ferroelectric phase transition in $\text{Cd}_2\text{Nb}_2\text{O}_7$ shows that (1) there is significant suppression of the dielectric constant by the application of dc electric field, (2) the electric-field dependence of the dielectric constant can be well described by modified Devonshire relation including a cluster term, i.e., $\epsilon(E) = \epsilon_1 - \epsilon_2 E^2 + \epsilon_3 E^4 + (Px/\epsilon_0) [\cosh(Ex)]^{-2}$. The polar clusters carry polarization $P = \sim 0.5 - 2.5 \text{ mC/m}^2$ and the cluster size, $L = \sim 11 - 15 \text{ nm}$ from 165 to 188 K. This indicates that mode I probably results from the cluster polarization.

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