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Effect of dc bias on dielectric properties of $Cd_2Nb_2O_7$ ceramics

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The effect of dc bias on dielectric properties of cadmium pyroniobate $Cd_2Nb_2O_7$ ceramics is studied in this article. Without dc bias, two obvious dielectric peaks around 80 and 180 K are observed; by applying dc bias, the two peaks are greatly suppressed and finally eliminated at 15 kV/cm, however, a peak with no frequency dispersion shows up at 192 K. The results show high electric-field tunability of the dielectric constant with a low dielectric loss at radio frequencies. The electric-field dependence of the dielectric constant around 80 K can be well described by the modified Devonshire relation including the Langevin-type cluster term, i.e., $\varepsilon(E)=\varepsilon_1-\varepsilon_2E^2+\varepsilon_3E^4+(P_jx_j/\varepsilon_0)\times[\cosh(Ex_j)]^{-2}$. The fit parameters indicate that the polar cluster carries polarization $P=\sim0.28-0.65\,\mathrm{mC/m^2}$ with the cluster size of $L=\sim24-30\,\mathrm{nm}$. [DOI: 10.1063/1.1388856]

I. INTRODUCTION

Cadmium pyroniobate, $Cd_2Nb_2O_7$ (CNO), shows an unusual ferroelectric behavior at low temperatures.[1–10] Two main dielectric anomalies in CNO ceramics were reported at first as indicated by measurement of the dielectric behavior in the temperature range 10–300 K.[1] Later its ferroelectricity was extensively studied by Isupov's,[2,3] Smolenskii's,[4–6] and Kolpakova's groups,[8–10] who reported that there are up to possibly eight phase transitions detected by the dielectric, light scattering, electro-optic, and specific heat measurements in CNO. Although the dc electric-field dependence of dielectric behavior of the CNO compound has been reported, a systematic investigation is still lacking.

Recently, field/frequency agile materials for microwave electronics have received great attention, in which it was demanded that a dielectric material have both a high dc electric-field tunability $K(=[\varepsilon(E_0)-\varepsilon(E)]/\varepsilon(E_0))$ and a low dielectric loss at microwave frequencies.[11–13] One of the most currently studied systems for this objective is the perovskite $SrTiO_3$ and related solid solutions.[13–16] $SrTiO_3$ single crystal shows a very high dc electric-field tunability at low temperatures and a reasonably low dielectric loss. However, it is found that the dielectric loss of $SrTiO_3$ increased greatly after it was made as a thin film.[16–18] This motivates us to revisit other dielectric materials, especially for the dielectric behavior under dc bias.

In this article we report the effect of dc electric fields on the dielectric behavior of $Cd_2Nb_2O_7$.

II. EXPERIMENTAL PROCEDURES

The ceramic samples of CNO were prepared by the solid state reaction. Complex dielectric constant was measured using HP 4284A LCR meters with the ac field of 2 V/mm. The temperature dependence of dielectric properties was measured in a cryostat system in the temperature range 10–300 K, while the specimen was being cooled or heated up at a typical cooling/heating rate of 1 K/min.

A dc voltage was applied to the samples and a blocking circuit was adopted to separate the high dc voltage and LCR meters. At each measuring temperature the sample was allowed to attain thermal equilibrium for 15 min before the field dependence of the dielectric constant and loss data were recorded.

III. RESULTS AND DISCUSSION

A. Temperature dependence of the dielectric constant and loss

The temperature dependence of the dielectric constant (ε) and the dielectric loss (tan δ) under dc electric field at 0.1, 1, 10, and 100 kHz is shown in Figs. 1 and 2. Without dc bias, the two dielectric peaks with obvious frequency dispersion occur at temperatures of ~180 and ~80 K. The dielectric relaxation behavior has been discussed in detail in Ref. 19. In addition, a dielectric anomaly at ~192 K is also observed in the temperature dependence of the $1/\varepsilon'$ (denoted as peak *A*).[19] In the literature, the dielectric anomaly at ~80 K was attributed to an "incommensurate–commensurate phase transition," while the anomaly around ~180 K was attributed to the "diffuse phase transition,"[3,6,10] and peak *A* was assigned as a "paraelectric–ferroelectric phase transition."[3,6,10] At high temperatures ($T>180\,\mathrm{K}$), i.e., in the paraelectric state, tan δ is small; at $T<180\,\mathrm{K}$, in the ferroelectric state, tan δ increases rapidly, and several relaxation peaks occur.

By applying dc electric field, a significant decrease in ε and tan δ is observed. First, the frequency dispersion of ε is suppressed under dc bias. Second, with increasing dc electric field, the two dielectric peaks around 80 and 180 K are greatly decreased, and finally eliminated at ~15 kV/cm. However, the peak around 192 K shows up, which is peak *A*. Third, peak *A* keeps almost the same inten-

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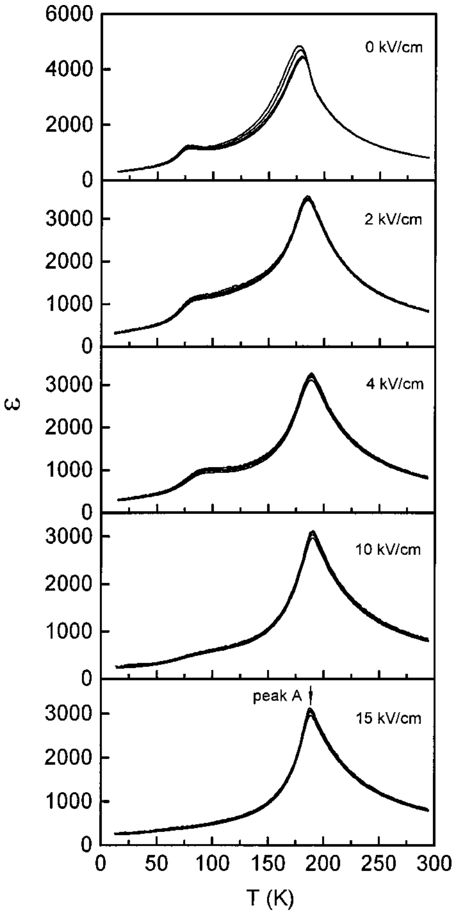

FIG. 1. Temperature dependence of ε at 0.1, 1, 10, and 100 kHz (from top to bottom) for $Cd_2Nb_2O_7$ ceramics under various dc electric fields.

sity and the same T_m in the electric-field range of 10–15 kV/cm.

These results indicate that the dielectric behavior of CNO without dc bias is the sum of peak A and the frequency dependent dielectric peaks at low temperatures. From this point of view, the dielectric behavior of CNO is similar to that of $(Sr,Bi)TiO_3$ solid solutions, which displays a sum effect of several dielectric defect modes and a ferroelectric relaxor mode.[20,21]

B. Field dependence of the dielectric constant and loss

The electric-field dependence of the ε and $\tan\delta$ around the two main dielectric peaks is shown in Figs. 3 and 4, respectively. It clearly shows that both ε and $\tan\delta$ decrease with increasing electric field from 0 to 10 kV/cm. For example, the dielectric maximum ($\varepsilon_{\max}=2500$) at 10 kV/cm is much lower than the value ($\varepsilon_{\max}=4500$) at zero electric field; the corresponding $\tan\delta$ decreases from 2×10^{-3} without dc bias to 4×10^{-4} at 10 kV/cm.

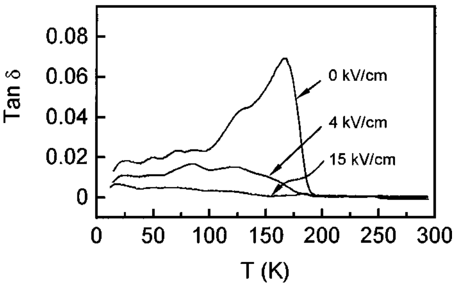

FIG. 2. Temperature dependence of $\tan\delta$ at 5 kHz for $Cd_2Nb_2O_7$ ceramics under various dc electric fields.

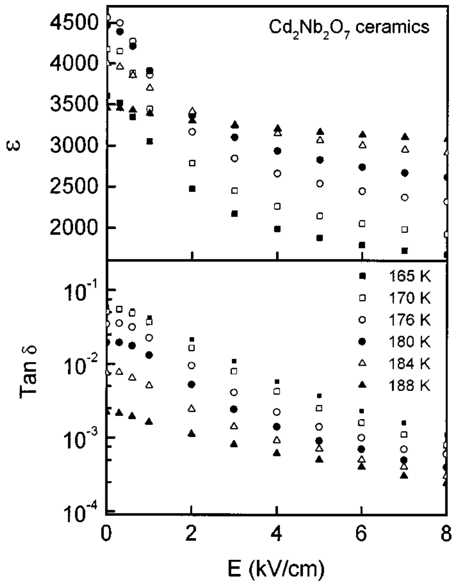

FIG. 3. The dc electric-field dependence of ε and $\tan\delta$ for $Cd_2Nb_2O_7$ ceramics at 5 kHz at temperatures around 180 K, the paraelectric–ferroelectric transition temperature.

The tunability (K) of the dielectric constant is calculated by the following equation:

$$K=[\varepsilon(E_0)-\varepsilon(E)]/\varepsilon(E_0), \tag{1}$$

where E_0 is the starting electric field, generally taking $E_0=0$ kV/cm, and E is the electric field at which we calculate the tunability. If taking $E_0=0$ kV/cm and $E=15$ kV/cm, the

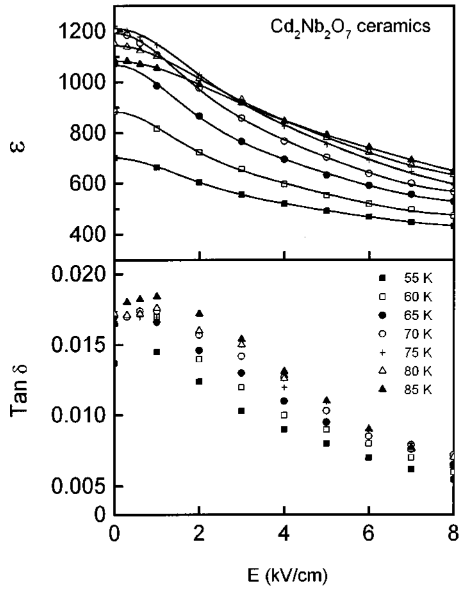

FIG. 4. The dc electric-field dependence of ε and $\tan\delta$ for $Cd_2Nb_2O_7$ ceramics at 5 kHz at temperatures around 80 K, the incommensurate–commensurate transition temperature. The solid curves are the fits to Eq. (2).

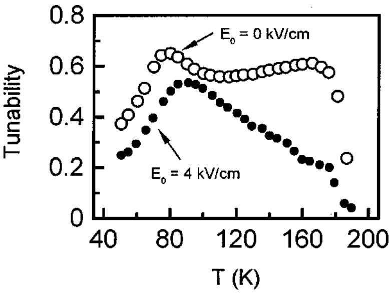

FIG. 5. Temperature dependence of the tunability $K(=[\varepsilon(E_0)-\varepsilon(E)]/\varepsilon(E_0))$ for $Cd_2Nb_2O_7$ ceramics under 15 kV/cm and 5 kHz for $E_0=0$ and 4 kV/cm, respectively.

tunability persists with high values between 37% and 64% in the temperature range 55–180 K. The temperature dependence of the tunability at 15 kV/cm and 5 kHz is shown in Fig. 5.

At 15 kV/cm tan δ is substantially low; especially in the temperature range of 150–180 K, tan δ is $(0.4-2)\times10^{-3}$. However, without dc bias, i.e., $E_0=0$ kV/cm, the dielectric loss is high. For example, in the temperature range 150–180 K, tan δ is $(0.4-6.7)\times10^{-2}$. However, if taking $E_0=4$ kV/cm, although the tunability is reduced to about 21%–50%, which is still reasonably high, as shown in Fig. 5, tan δ is $(1-9)\times10^{-3}$ at 4 kV/cm from 150 to 180 K, much lower than those obtained at $E_0=0$ kV/cm.

The above results indicate that CNO displays a high tunability and a reasonably low tan δ under dc bias. This compound might be a candidate material for the frequency/field agile material application.

C. Fits to the modified Devonshire relation

In the previous paper of the present authors,[22] we reported that the electric-field dependence of ε around 180 K can be well fitted to the modified Devonshire relation including the Langevin-type cluster term,[22–25]

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

where $x=PL^3/(2k_BT)$ with the cluster polarization P and size L. ε_1, ε_2, ε_3, and ε_0 designate the linear, nonlinear, high-order dielectric constant, and that of vacuum, respectively. The three leading terms on the right-hand side of Eq. (2) describe the conventional linear and nonlinear dielectric response up to the order of E^4, which corresponds to the conventional electric-field dependence of ε of a displacive-type polar system in the paraelectric regime. The fourth term on the right-hand side of Eq. (2) describes the contribution from the possible polar clusters. In this article we adopt the same scenario to analyze the electric-field dependence of ε around 80 K.

The fitting curves (solid curves) around 80 K are shown in Fig. 4. It shows that the fitting curves are in good agreement with the experimental data. The detailed fitting curves at three typical temperatures are shown in Fig. 6. It can be seen that the contribution of the polar-clusters to ε is about 22% without dc bias at 55 K $(T<T_m)$. At 70 K, near the T_m, the contribution of polar clusters is about 30%. The contribution of polar clusters to ε is significant below ~5 kV/cm, while it almost disappears at the high electric fields higher than 6 kV/cm. At 85 K, slightly higher than the T_m, the contribution of the polar clusters decreases to about 19% without dc bias.

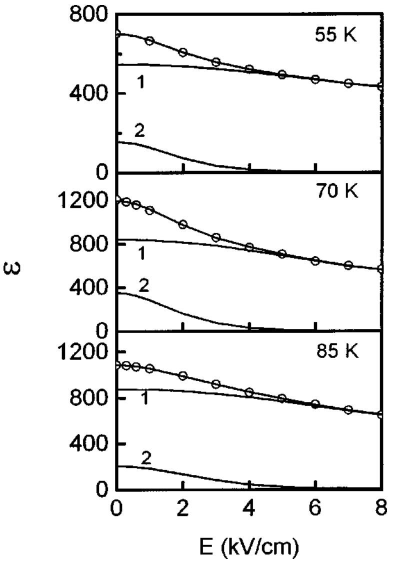

FIG. 6. The dc electric-field dependence of ε for $Cd_2Nb_2O_7$ ceramics at 55, 75, and 85 K. The symbols: experimental data; the solid curves: the fits to Eq. (2); curve 1 is the contribution from the conventional polarization terms and curve 2 is the contribution from the Langevin-type cluster term.

The obtained parameters ε_1, ε_2, and ε_3 as a function of temperature are shown in Fig. 7(a). The temperature dependence of the linear dielectric constant ε_1 and nonlinear terms ε_2 and ε_3 reveal that a peak occurs at ~75 K, which is in agreement with T_m observed under zero electric field. The size and polarization of the polar clusters obtained by fitting are shown in Fig. 7(b). The polar clusters carry the polarization $P=\sim0.28-0.65\,\mathrm{mC/m^2}$ with the clusters size $L=\sim24-30\,\mathrm{nm}$. Compared with the parameters obtained

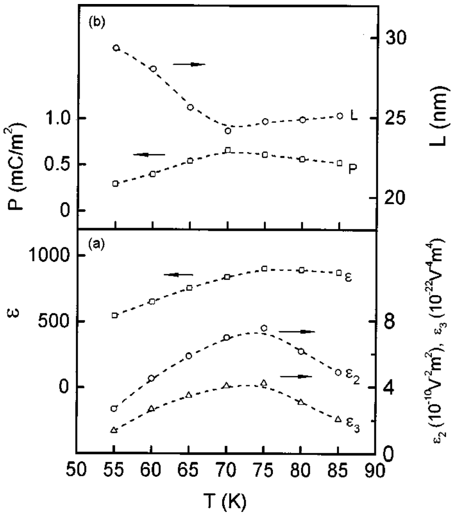

FIG. 7. (a) Temperature dependence of the linear dielectric constant ε_1 and the nonlinear terms ε_2 and ε_3. (b) Temperature dependence of the polar-cluster polarization (P) and size (L); obtained by the best fits of the dc electric-field dependence of ε to Eq. (2).

around 180 K, the polarization is smaller and the polar-clusters size is larger; this is reasonable because the dielectric peak occurs at a lower temperature. However, the real physical meaning of the Langevin-type polar-cluster term in the present work is still not clear, which needs further study.

IV. CONCLUSION

By applying dc electric field, significant suppression of ε and $\tan\delta$ is observed. The dielectric anomalies around 80 and 180 K are greatly suppressed, and finally eliminated at 15 kV/cm; however, a peak with no frequency dispersion shows up at 192 K. The electric-field dependence of ε around 80 K can be well described by the modified Devonshire relation including the Langevin-type cluster term, i.e., $\varepsilon(E)=\varepsilon_1-\varepsilon_2\ E^2+\varepsilon_3\ E^4+(Px/\varepsilon_0)[\cosh(Ex)]^{-2}$. The calculated parameters are the polarization $P=\sim 0.28$–$0.65\,\mathrm{mC/m^2}$ and the cluster size $L=\sim 24$–$30\,\mathrm{nm}$ from 55 to 85 K.

The high electric-field tunability with a low dielectric loss is obtained at radio frequencies. This implies that the CNO compound might be a promising candidate for field/frequency agile materials application. Further studies on the effect of electric field on the dielectric behavior at microwave frequencies, and the further improvement of the dielectric properties through doping, are needed.

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