

Phase-transition temperature and character of $\text{Cd}_2\text{Nb}_2\text{O}_7$ Chen Ang^{1,2} and Zhi Yu¹¹Department of Physics, The University of Akron, Akron, Ohio 44325, USA²Department of Chemistry, The University of Akron, Akron, Ohio 44325, USA

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The complicated dielectric spectrum of $\text{Cd}_2\text{Nb}_2\text{O}_7$ around the “paraelectric-ferroelectric” (PF) phase transition is greatly simplified due to the suppression of the multiple dielectric relaxation processes under a dc electric field. The PF transition is revealed under a dc electric field and characterized by the Curie-Weiss relation. The results show that the PF phase transition is of second order. The dc electric field influence on the dielectric relaxation modes and PF phase transition for both single crystals and ceramics is discussed.

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I. INTRODUCTION

The ferroelectricity of $\text{Cd}_2\text{Nb}_2\text{O}_7$ (CNO) compound was reported in 1952.¹ Among thousands of ferroelectrics, CNO has been recognized as an unique one due to its peculiar polarization behavior, including the existence of several overlapped dielectric anomalies, an unusual dielectric behavior under dc bias, and the coexistence of the ferroelastic and ferroelectric effect.^{1–4} Great effort has been devoted to the understanding of the polarization mechanism of CNO.^{5–17} However, to date, some basic subjects are still unclear, such as (1) which dielectric anomaly reflects the “paraelectric-ferroelectric” (PF) phase transition and (2) whether the phase transition is of first order^{5,8} or second order.^{9,10}

One of the main difficulties in clarifying these questions is that many polarization processes coexist; for example, there are three dielectric anomalies over a narrow temperature range from 195 to 205 K, including the possible PF phase transition.^{2–4,7} The coexistence of multiple polarization processes causes complexity in resolving at which temperature the phase transition happens and what is the physical nature of each dielectric anomaly. One of traditional methods for determining the order of the PF phase transition using the ratio criteria of $1/\varepsilon$ vs T slopes obtained from the Curie-Weiss relation at $T > T_c$ and $T < T_c$ cannot be applied to this case.

On the other hand, the temperatures (T_m) where the dielectric anomalies (including the PF phase transition) occur depend sensitively on the condition of measurement, such as cooling or heating cycles, different heating and cooling rates, and the quality of samples (ceramics, single crystal, or with different defects). For different samples or the same sample measured at different cycles and rates, T_m might have $\geq \sim 10$ K difference for the same dielectric anomaly.

In the present work, we report the dielectric behavior of CNO ceramics and single crystals under a dc electric field from 0 to 15 kV/cm. It is found that all the dielectric polarization processes except an “intrinsic” paraelectric-ferroelectric phase transition are eliminated under high dc fields and thus provide a good condition to determine the temperature where the “intrinsic” phase transition occurs and to better understand the physical nature of the observed dielectric anomaly.

II. EXPERIMENTAL PROCEDURE

The complex dielectric permittivity of CNO ceramic and single-crystal samples was measured by an HP 4284A LCR meter with an 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 at a cooling or heating rate of 1 K/cm. A dc voltage was applied to the samples and a blocking circuit was adopted to separate the high dc voltage from LCR meters.

III. RESULTS AND DISCUSSION

A. Temperature dependence of dielectric behavior without a dc field

The temperature dependence of the dielectric constant (ε) and dissipation factor ($\tan \delta$) for the CNO ceramic sample measured at both *cooling and heating cycles* is shown in Fig. 1. The CNO ceramic sample exhibits a complicated dielectric response, consisting of dielectric relaxation modes I, II, and III and peaks A and B. The trace of peak A can be seen

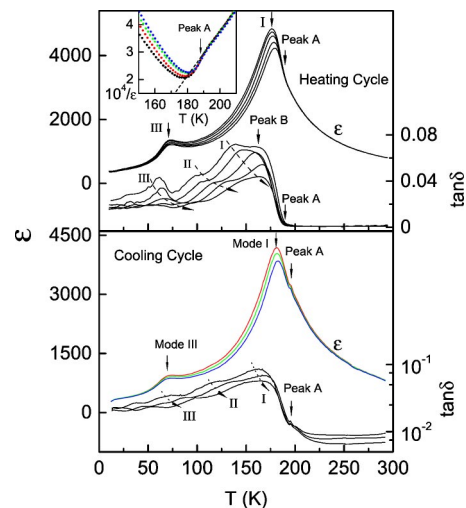


FIG. 1. Temperature dependence of the dielectric constant (ε) and dielectric loss ($\tan \delta$) of $\text{Cd}_2\text{Nb}_2\text{O}_7$ ceramics at both cooling (at 1, 10, and 100 kHz) and heating cycles (at 0.1, 1, 10, 100, and 1000 kHz).

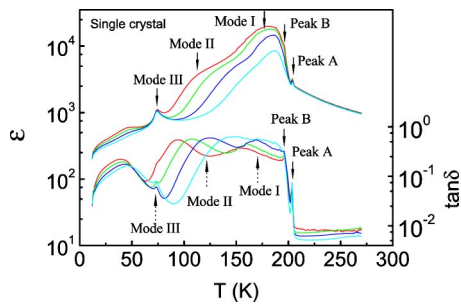


FIG. 2. Temperature dependence of ε and $\tan \delta$ for $\text{Cd}_2\text{Nb}_2\text{O}_7$ single crystals measured at a cooling cycle at 0.1, 1, 10, and 100 kHz.

in the temperature dependence of $1/\varepsilon$ as shown in the inset of Fig. 1 at the heating cycle, and the peak is more clearly shown at the cooling cycle. Peak B shows a shoulder in $\tan \delta$.

Similar behavior is observed in single crystals. Figure 2 shows the temperature dependence of ε and $\tan \delta$ measured for CNO single crystals. The three dielectric modes I, II, and III and peaks A and B have been observed. This is consistent with reports in the earlier literature.^{2-4,7} Compared with those of ceramic samples, peak B is clearly seen for single crystals.

Mode I has an apparent highest dielectric constant in the temperature range of 10–300 K. To date, which dielectric anomaly is the PF phase transition is still a subject of controversy. In Ref. 16, the authors attributed mode I to the PF phase transition (or say “diffuse” phase transition). But in Ref. 7, the authors attributed mode I to a polydispersion relaxation, peak B as a PF phase transition, and peak A as an improper PF and also an improper paraelastic to ferroelastic transition.

B. Temperature dependence of dielectric behavior under a dc field

The temperature dependence of ε for CNO ceramic sample under dc bias measured at a heating cycle is shown in Fig. 3(a). Under dc bias, the three dielectric relaxation processes (modes I, II, and III) are greatly suppressed or eliminated; at 15 kV/cm, modes I, II, and III fully disappear.

The remaining peak A can be further confirmed from the results measured at a cooling cycle, as shown in Fig. 3(b). At 3 kV/cm, the contribution from mode I is suppressed, and peak A is revealed.

More details can be observed for the evolution of the dielectric anomalies from the data of single crystals under dc bias measured at a heating cycle shown in Fig. 4. At 10 kV/cm, mode I is suppressed. At 15 kV/cm, both mode I and peak B are greatly eliminated and only peak A survives with less frequency dependence.

The complete suppression of mode I under dc bias in this work indicates that this mode is not a PF phase transition, which confirms the designation of a polydispersion relaxation for this dielectric anomaly in Refs. 7 and 11. In addition, peak B, being attributed to a sharp PF phase transition in Ref. 7, is also completely removed under the electric field,

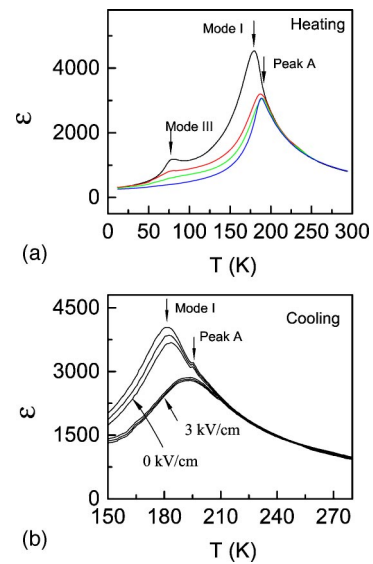


FIG. 3. (a) Temperature dependence of the dielectric constant (ε) of $\text{Cd}_2\text{Nb}_2\text{O}_7$ ceramics at 5 kHz under dc electric field of 0, 4, 8, 15 kV/cm (from top to bottom) at a heating cycle. (b) Temperature dependence of the dielectric constant (ε) of $\text{Cd}_2\text{Nb}_2\text{O}_7$ ceramics under dc electric field of 0 and 3 kV/cm at a cooling cycle at 1, 10, and 100 kHz (from top to bottom).

which excludes the possibility of a PF phase transition.

In fact, only peak A remains in both ceramic samples and single crystals at high electric field, for example, at 15 kV/cm. This strongly suggests that peak A is the PF phase transition, and its frequency independence behavior supports this assignment.

C. Order of the PF phase transition

The temperature dependence of ε at 15 kV/cm is plotted in Fig. 5(a) at 0.1, 1, 10, and 100 kHz, where the dielectric anomaly peak A remains and exhibits no frequency dispersion. The reciprocal dielectric constant ($1/\varepsilon$) of the CNO ceramic sample at 0 and 15 kV/cm as a function of temperature is shown in Fig. 5(b). The experimental data at

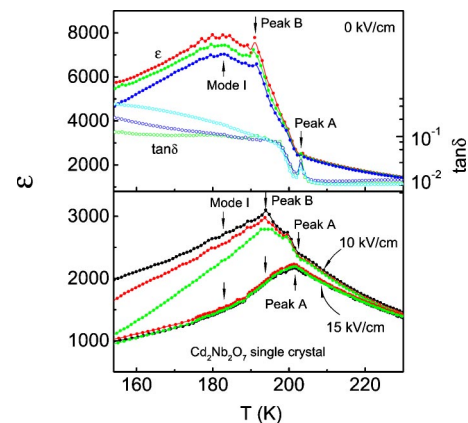


FIG. 4. Temperature dependence of ε and $\tan \delta$ for $\text{Cd}_2\text{Nb}_2\text{O}_7$ single crystals measured at a heating cycle at 0, 10 and 15 kV/cm at 1, 10, and 100 kHz.

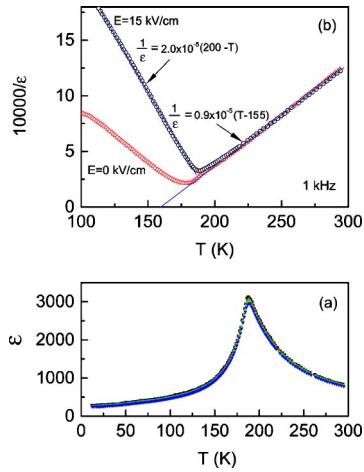


FIG. 5. (a) Temperature dependence of ϵ under dc field of 15 kV/cm at 0.1, 1, 10, and 100 kHz (the curves merge into one curve showing no frequency dispersion). (b) Temperature dependence of $1/\epsilon$ under dc bias of 15 kV/cm at 1 kHz for $\text{Cd}_2\text{Nb}_2\text{O}_7$ ceramics; for comparison, $1/\epsilon$ under zero dc field was also given (dots, experimental data; lines, fitting curves).

15 kV/cm were fitted to the Curie-Weiss relation at $T > T_c$,

$$1/\epsilon = \beta_1(T - \Theta_1), \quad (1)$$

with $\beta_1 = 0.9 \times 10^{-5}$ and $\Theta_1 = 155$ K. The Curie constant $C = 1/\beta_1 = 1.15 \times 10^5$ K. At $T < T_c$, the data fit to the relation

$$1/\epsilon = \beta_2(\Theta_2 - T), \quad (2)$$

with $\beta_2 = 2.0 \times 10^{-5}$ K and $\Theta_2 = 200$ K.

In the simplest case, the slope ratio above and below T_c for the reciprocal ϵ could be $\beta_2 = 2\beta_1$ and $\Theta_1 = \Theta_2$ for the *second-order* phase transition of normal ferroelectrics according to the Landau theory. However, for the *first-order* phase transition, the slope ratio is $\beta_2 = 8\beta_1$, and $\Theta_1 < \Theta_2$.¹⁸

The fitting to the dielectric data obtained under 15 kV/cm shows that $\beta_2 = 2.36\beta_1$, close to the expected β_2/β_1 ratio 2 for the *second-order phase transition*.

In addition, a more careful comparison between the dielectric data obtained at the cooling and heating cycles under 15 kV/cm indicates no thermal hysteresis occurs, and thus the possibility of the first-order type of phase transition can be excluded and the *second-order type* of phase transition for peak A is further supported.

Landau theory also predicts that the dielectric constant at T_c is infinite and $\Theta_1 = \Theta_2$ in an ideal material with a second-order phase transition. In the present work, the maximum of the dielectric constant (ϵ_{\max}) is ~ 3200 at 15 kV/cm ($\epsilon_{\max} = \sim 4500$ without dc bias) and $\Theta_1 (= 155 \text{ K}) < \Theta_2 (= 200 \text{ K})$. Obviously, the present dielectric behavior deviated from the predicted values of the Landau theory for the second-order phase transition. It is reported¹⁹ that the obvious deviation from the predicted values of the Landau theory is caused by impurity doping and defects such as porosity in the samples. In the present work, some unavoidable impurities and porosity could exist in the samples and this could be a possible reason for the suppression of the dielectric polarization.

In the literature, Kolpakova *et al.* attributed the phase

transition in CNO to the *first-order phase transition* in 1987 based on the β_2/β_1 slope ratio criteria and Curie temperatures Θ_1 and Θ_2 under a uniaxial stress.⁵ However, from Fig. 6 in Ref. 5, it can be seen that the dielectric constant profile is composed of the superimposition of the several peaks (at least two peaks); in this case, it is difficult to obtain precise data about slopes (β_2, β_1) and Curie temperatures (Θ_1, Θ_2).

On the other hand, Kolpakova *et al.*¹⁰ reported the *second-order nature of the PF phase transition* in 1996 based on a wide thermal anomaly observed by the differential thermal analysis. This is consistent with our conclusion in the present work. However, again, the overlapped dielectric polarization mechanism in the temperature range makes the conclusion not convincing based only on a thermal hysteresis in wide temperature range.¹⁰ In addition, Salaev *et al.* pointed out that the phase transition is of second order in 1992.⁹

In the present work, by taking the advantage of the complete suppression of other dielectric polarization processes, a conclusion that the PF transition is of a *second-order phase transition* could be drawn.

One argument may be raised that the data obtained under 15 kV/cm may not really reflect the paraelectric-ferroelectric peak at zero field, because the dc field may have influence on the peak. For example, CNO is very probably a system close to the tricritical point.²⁰⁻²² This explains why there is the controversy over whether it is a first- or second-order phase transition. In this case, there are two possibilities: (1) The paraelectric-ferroelectric phase transition peak A at zero field is the first-order phase transition; then, it is converted into the second-order phase transition under 15 kV/cm, as the material is the system close to the tricritical point. (2) The paraelectric-ferroelectric phase transition peak A at zero field is the second-order phase transition; peak A does not change much and still remains in the second-order phase transition under dc bias, up to 15 kV/cm. Indeed, it is difficult to obtain clear information of the paraelectric-ferroelectric phase transition at zero field due to the superimposition of the other dielectric modes if the phase transition can be easily affected by applied dc bias as a tricritical-point system.

It is noticed that the dc field has very weak effect on peak A in a wide field range (0–30 kV/cm). This is one of the special characteristics of CNO. Especially, it is noted that the T_{mA} is almost the same with increasing dc electric field as presented in Figs. 3 and 4, and it is also the same even at 20 and 30 kV/cm (not shown here). This phenomenon implies that the phase transition nature is less influenced by the dc field (at least ≤ 15 kV/cm), and the characterization of the PF transition at 15 kV/cm becomes a reasonably good approximation for the behavior at zero dc electric field.

Obviously further work is needed to clarify this issue, for example by measuring a series of critical exponents of the phase transition to examine if CNO is truly a tricritical system and carrying out a comparison of the dielectric behavior under different dc fields.

In addition, why does the dc electric field have a very weak effect on T_m of the PF transition? A possible explanation is the following. According to the phenomenological theory, considering a standard treatment, the relation be-

tween polarization and electric field can be described as

$$E = AP + BP^3 + CP^5 + \dots \quad (3)$$

In a second-order phase transition, only the coefficient A may have a negative value. There is one positive solution of polarization P at $E > 0$. Under dc bias, the T_m is shifted to a higher temperature following the relationship¹⁸

$$\Delta T = k E^{2/3}. \quad (4)$$

In the present work, the almost unshifted T_m implies that the coefficient k is very small. For details, further study is needed.

The results obtained in this work indicate that the “unusual” dielectric behavior could probably be understood by application of a dc field; the extrinsic dielectric relaxation processes can be eliminated by the dc field and only the intrinsic PF phase transition remains. In addition, the applied electric field is not very high (for example, less than 15 kV/cm); the PF phase transition seems to be almost the same as it is at zero field. This provides a good condition to study the physical nature of the PF phase transition. For example, a description by the phenomenological theory for CNO becomes possible in this case. Further work is being conducted.

IV. CONCLUSIONS

In conclusion, the dielectric behavior of CNO under dc electric field demonstrates that the dielectric anomaly peak A at ~ 201 K for the single crystals or at 196 K for ceramics is due to the “paraelectric-ferroelectric” phase transition. With increasing electric field, only this anomaly remains, while the dielectric relaxation processes are greatly suppressed. The complete elimination of the dielectric anomalies, peak B (only for single crystals), modes I, II, and III under dc bias (~ 15 kV/cm) indicates that these dielectric anomalies are not the “paraelectric-ferroelectric” phase transition. Based on analysis of the dielectric constant using the Curie-Weiss relation and comparison of the data obtained from measurements at cooling and heating cycles, it is suggested that the “paraelectric-ferroelectric” phase transition is of second-order nature.

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