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Ferroelectricity in $\text{H} \cdot \text{NH}_4(\text{ClCH}_2\text{COO})_2$

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$\text{H} \cdot \text{NH}_4(\text{ClCH}_2\text{COO})_2$ is ferroelectric below -145°C . At room temperature, the crystal is monoclinic with $a=10.56$, $b=11.51$, $c=8.36$ Å, $\beta=119^\circ 50'$, and space group is most probably $C2/c$. The density is 1.528 g/cm³. The unit cell contains four formula units. The ferroelectric axis is along the $[102]$ direction. The spontaneous polarization is 0.18 μC/cm² and the coercive field is 1.2 kV/cm at -195°C . Along the ferroelectric axis the dielectric constants obey the Curie-Weiss law with a Curie-Weiss constant of 44°C . The domain-wall motion seems to contribute to the initial dielectric constants if the frequency of applied ac field is as low as 10 kc/sec. The phase transition seems to be of the first order.

I. INTRODUCTION

IN 1957 Pepinsky *et al.*¹ found that ammonium monochloroacetate, $\text{ClCH}_2\text{COONH}_4$, crystallizes in two forms. Form I is orthorhombic with space group $P2_12_12_1$ and form II is monoclinic with space group $C2/c$, at room temperatures. Form II exhibited ferroelectricity below -150°C . Pepinsky *et al.* reported, however, that they succeeded in growing form-II crystals only once, and conditions for growing the crystals and details of their properties are not known. The primary purpose of the present study was to find a method of growing form-II crystals reproducibly. During the study, however, we have found a new ferroelectric crystal, properties of which will be described below.

II. CHEMICAL COMPOSITION AND CRYSTAL PARAMETERS

Ammonium monochloroacetate was prepared around 0°C by passing dry NH_3 gas into water-free monochloroacetic acid dissolved in pure ethyl ether. The compound was then dissolved in methyl alcohol. The solution usually shows acidity, presumably because of remaining monochloroacetic acid. Its pH was controlled by adding NH_4OH or ClCH_2COOH . The evaporation method was used to grow crystals, keeping the temperature at -5°C . Orthorhombic crystals were grown from a solution the pH of which was more than 5.3 , whereas monoclinic crystals were obtained from a solution of pH 4.5 . The lattice constants of the orthorhombic

¹R. Pepinsky, Y. Okaya, and T. Mitsui, *Acta Cryst.* **10**, 600 (1957).

crystals were close to those of the form I of Pepinsky *et al.*, suggesting that these two are the same.

The monoclinic crystals have unit-cell parameters of $a=10.56$, $b=11.51$, $c=8.36$ Å, $\beta=119^\circ 50'$. The systematic extinction of Bragg reflections proved that the space group is $C2/c$ or Cc . Density measurements were made by the air-comparison method at 18°C using a Beckman-Toshiba 930-type pycnometer, and the value of 1.528 g/cm³ was obtained. An elementary analysis of the orthorhombic crystal gave the weight percentages of C, H, and N corresponding to the chemical formula of $\text{ClCH}_2\text{COONH}_4$, which was given to form I by Pepinsky *et al.* For the monoclinic crystal an analysis gave the weight percentages C=23.01%, H=4.25%, N=7.08%. Possible chemical formulas, such as $\text{ClCH}_2\text{COONH}_4$ plus water of crystallization etc., were examined and the best agreement was found for $\text{H} \cdot \text{NH}_4(\text{ClCH}_2\text{COO})_2$, for which C=23.30%, H=4.37%, N=6.80%. Infrared absorption spectra show absorptions characteristic to the NH , CO_2 , and CCl bond vibrations, supporting the above conclusion on the chemical formula. The unit-cell dimension and density suggest that the unit cell contains four formula units. The monoclinic crystals could be obtained reproducibly from the methyl-alcohol solution with pH 4.5 .

III. FERROELECTRIC PROPERTIES

Ferroelectric hysteresis loops were observed in the $[102]$ direction by applying a 50-cps ac field below -145°C . An example is shown in Fig. 1. The maximum value of the spontaneous polarization was observed in

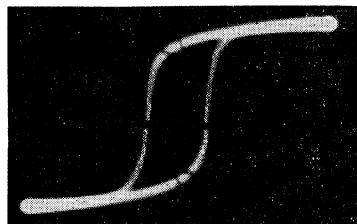


FIG. 1. A hysteresis loop observed along the $[102]$ direction at -170°C .

the $[102]$ direction and no hysteresis loops were observed in the direction perpendicular to the $[102]$. Therefore, the spontaneous polarization seems to be parallel to the $[102]$. The dielectric constants ϵ for the applied field of 10 kc/sec and 0.4 V/cm are shown as a function of temperature in Fig. 2. The dielectric constant is 5.9 at room temperature. This value remains constant down to about -145°C , where the dielectric constant suddenly jumps to a high value of about 1.2×10^3 . As the temperature is further lowered to about -160°C , the dielectric constants decrease to nearly the same value as at the room temperatures. Just below the transition temperature, a small disagreement was observed between the dielectric constants measured with increasing and decreasing temperatures, even when the rate of cooling or warming was as small as $0.2^{\circ}\text{C}/\text{min}$. The dielectric constants obey the Curie-Weiss law above the transition temperature with a Curie constant

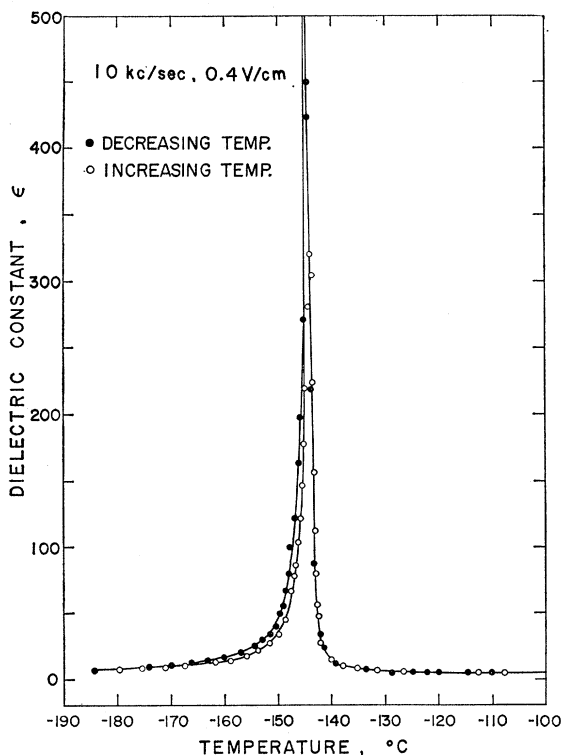


FIG. 2. The dielectric constant along the $[102]$ direction as a function of temperature.

of 44°C and a paraelectric Curie temperature very close to -145°C . Figure 3 shows dielectric constants along the $[1\bar{1}0]$ and the $[110]$ directions, which are nearly perpendicular to the ferroelectric $[102]$ direction. As seen in the figures, only small bumps appear near the Curie point.

The shape of the dielectric-constant-versus-temperature curve shown in Fig. 2 is similar to those of $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{BeF}_4$, and $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$ recently studied in detail by Ohshima and Nakamura.² Just below the transition point the dielectric constant is reduced significantly by applying a dc bias field of 12 kV/cm, whereas practically no change was observed above the transition temperature, as shown in Fig. 4. The peak value of the dielectric constant was reduced to

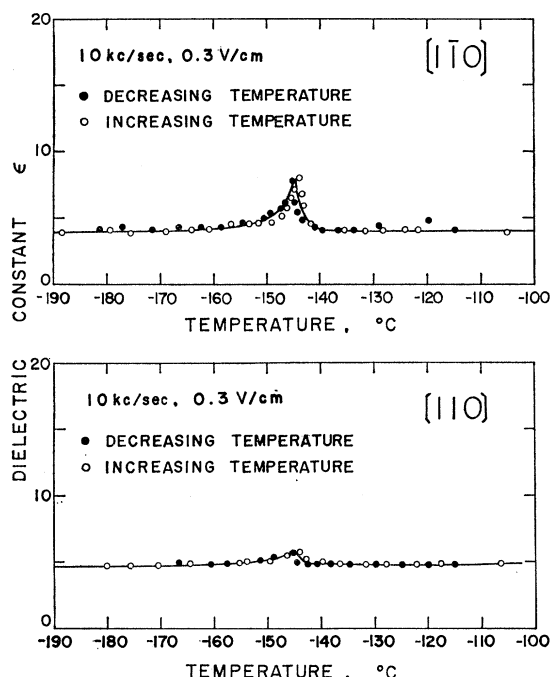


FIG. 3. The dielectric constants along the $[1\bar{1}0]$ and the $[110]$ directions as functions of temperature.

34 at the Curie point by the bias field. This behavior is again quite similar to that of $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{BeF}_4$, and $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$. These results suggest that the domain-wall motion contributes to the initial dielectric constant in $\text{H}\cdot\text{NH}_4(\text{ClCH}_2\text{COO})_2$ as in the cases of $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{BeF}_4$, and $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$. Presumably a difference in the domain structure could be a cause of the above-described difference between the dielectric constants measured with increasing and decreasing temperatures. Figure 5 shows the temperature dependence of the spontaneous polarization measured along the $[102]$ direction. At the Curie point the spontaneous polarization jumps to about $0.05 \mu\text{C}/\text{cm}^2$ and reaches $0.18 \mu\text{C}/\text{cm}^2$ at -195°C . The discontinuous

² H. Ohshima and E. Nakamura, J. Phys. Chem. Solids **27**, 481 (1966).

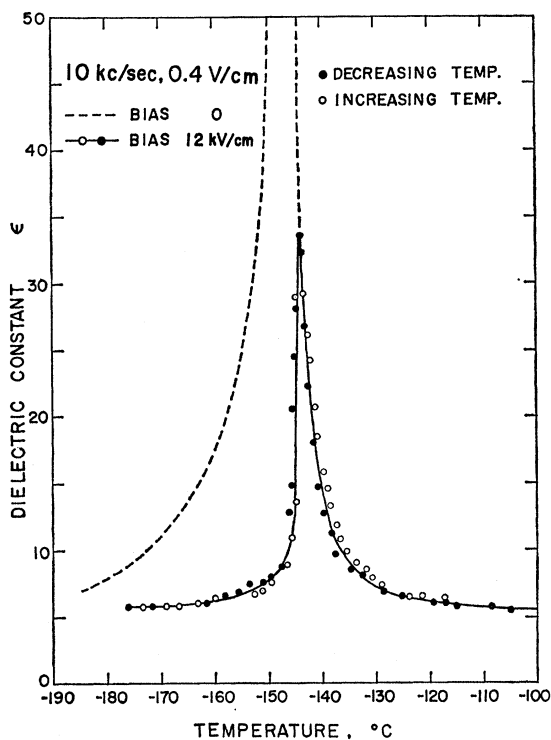


FIG. 4. The dielectric constants ϵ measured along the $[102]$ direction with the 12-kV/cm dc bias field in comparison with those for no bias.

changes in the spontaneous polarization and the dielectric constant (Fig. 4) suggest that the phase transition is of the first order. The double hysteresis loop characteristic of the first-order transition, however, was not observed above the Curie point. Figure 6 shows

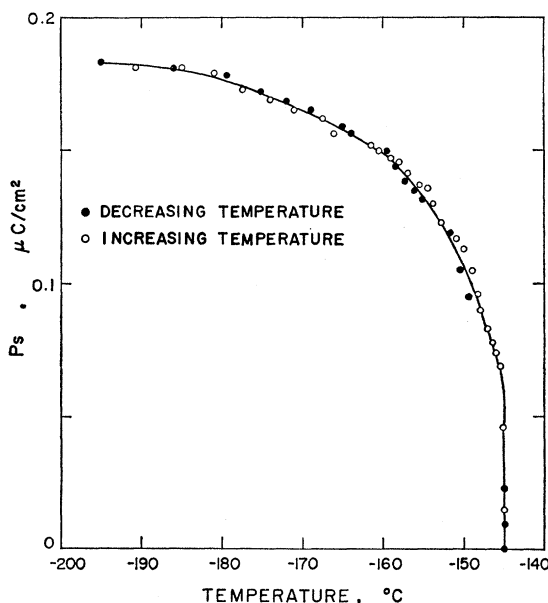


FIG. 5. The spontaneous polarization P_s along the $[102]$ direction as a function of temperature.

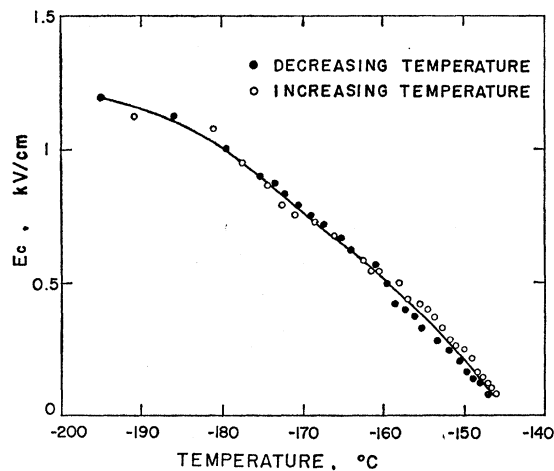


FIG. 6. The coercive field E_c along the $[102]$ direction as a function of temperature.

the temperature dependence of the coercive field. Its value is smaller than in the usual ferroelectrics.

IV. DISCUSSION

As described in Sec. II, the space group of $H \cdot NH_4(ClCH_2COO)_2$ is $C2/c$ or Cc at room temperature. The space group Cc , however, corresponds to the pyroelectric crystal symmetry, and therefore the most probable space group is $C2/c$ at room temperature, and presumably Cc below the Curie point. These are the same as those of the form II crystal of Pepinsky *et al.*³ The Curie point (-145°C) and the order of magnitude of the spontaneous polarization ($0.18 \mu\text{C}/\text{cm}^2$ at -195°C) of our crystal are close to those of form II (-150°C and $0.1 \mu\text{C}/\text{cm}^2$, respectively).¹ The results of the chemical analysis, the lattice parameters and the density ($1.528 \text{ g}/\text{cm}^3$ compared to $1.5585 \text{ g}/\text{cm}^3$ of the form II), however, prove that our crystal is definitely different from the form II of Pepinsky *et al.* The dielectric properties of our crystal are similar to $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$, and $(NH_4)_2Cd_2(SO_4)_3$ in the following respects: The phase transition seems to be of the first order, the Curie-Weiss constant is small, and the domain-wall motion seems to contribute to the initial dielectric constants. An x-ray structure analysis of the crystal is being made by one of the present authors (M. I.).

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³ R. Pepinsky, K. Vedam, and Y. Okaya, Phys. Rev. **110**, 1309 (1958).

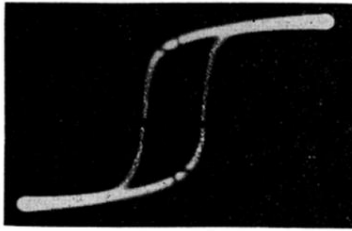


FIG. 1. A hysteresis loop observed along the $[102]$ direction at -170°C .